

STUDIES ON THE CONSTITUTION OF SHONANIC ACID, ONE  
OF THE TWO CHARACTERISTIC VOLATILE ACIDS FROM  
THE WOOD OF LIBOCEDRUS FORMOSANA, FLORIN.

I. THE ISOLATION OF SHONANIC ACID AND  
ITS GENERAL PROPERTIES.

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*Libocedrus formosana*, Florin or "Shōnan-Boku" is a conifer indigenous to Formosa and its older growths are found along the northern part of the central mountain range at an altitude of 300-1200 m. above sea level. The heartwood is of somewhat light brown colour and bears a characteristic spicy odour and is highly resistant against the attack of the white ant, but as to the nature of its volatile constituents nothing had been known till Kinzō Kafuku and his collaborators studied the volatile oil of this wood from the standpoint of anti-white-ant materials. They distilled the wood chopped into small slices with steam and subsequently extracted the distillate with ether. The oil thus obtained had the following properties:  $d_{4}^{20}$  1.0318;  $n_D^{20}$  1.4956;  $\alpha_D + 3.20^\circ$ ; acid value 295.8; ester value 5.4.

This oil was found to consist of 89% acidic, 6% phenolic, and 5% neutral, substances and the presence of a new acid of the formula  $C_{10}H_{14}O_2$  melting at  $103^\circ C$ . was shown, but as to the nature of this acid nothing has been reported and the chemistry of the substance was left untouched for about 6 years ever since. The present author, with a view to studying the acid, extracted the sliced wood, about  $3 \times 10 \times 15$  cm. in size, with a slight excess of sodium hydroxide solution and obtained a quantity of the material for examination. The yield of the volatile substances amounted nearly to 0.45% on the average and the product represented a reddish brown mobile fluid of the characteristic odour. The material was found to consist of 95% acidic and 5% phenolic substances and in the acidic portion there was shown the presence of at least three distinct crystalline substances, melting at  $40-41^\circ$ ,  $78-81^\circ$ , and  $103^\circ$ , respectively.

The acid melting at  $103^\circ$  proved to be identical with the acid formerly obtained by Kafuku but its yield was not so rich as in the previous case. Thus the expectation of the present author to get a sufficient quantity of this acid for his investigation was not realized, but in its stead he could obtain a quantity of another acid melting at  $40-41^\circ$ , also an unknown substance of the

formula  $C_{10}H_{14}O_2$ , its amide melting at  $116-117^\circ$  and anilide at  $111-112^\circ$ , respectively.

To this substance, which has never been described, the author gave the name "shonanic acid" and this paper deals with the chemistry of the new acid. The author, after a series of experiments, has at last succeeded in clearing up the structure of this acid, the detailed account of which will be reported in the following.

Shonanic acid  $C_{10}H_{14}O_2$ , when reduced catalytically with hydrogen and palladium on barium sulphate, absorbs 4 atoms of hydrogen giving rise to tetrahydroshonanic acid ( $C_{10}H_{18}O_2$ ), but if alcohol and sodium (2 to 3 times of the required amount of sodium for the production of dihydroshonanic acid  $C_{10}H_{16}O_2$  (1)) be used for reduction it gave dihydroshonanic acid  $C_{10}H_{16}O_2$ , showing that the two double bonds are conjugated. This dihydro-acid, on further reduction, can be transformed into tetrahydroshonanic acid  $C_{10}H_{18}O_2$ . The melting points of the amides of shonanic-, dihydroshonanic-, and tetrahydroshonanic acids are  $116-117^\circ$ ,  $130-131^\circ$ , and  $144-145^\circ$ , respectively.

On consulting the literature, we find among the amides of saturated monocyclic acids of the formula  $C_{10}H_{18}O_2$ , dihydro- $\alpha$ -campholenic amide melting at  $143-144^\circ$  (1), which is very near that of tetrahydroshonanic amide.

In order to ascertain whether or not tetrahydroshonanic acid is identical with dihydro- $\alpha$ -campholenic acid, the latter was prepared from camphor (see the experimental part) and on examining the melting point of the mixture of their amides, it was found that they were quite different.

Although the formation of tetrahydroshonanic acid on catalytic reduction reveals the presence of two double bonds in shonanic acid, it absorbs but two atoms of bromine. This may be attributed to the conjugation of the two ethylene linkages, as seen from the behaviour of butadiene (2), hexadiene-(2, 4) (3), diphenyl-butadiene (4), phellandrene (5), sorbic acid (6), cinnamylidene-malonic ester (7), cinnamylidene-acetic acid (8), crotonylidene-malonic ester (9), and phenyl-cinnamenyl-acrylic acid (10), which, though differing in the modes of addition, absorb only two atoms of bromine. The existence of the conjugated double bonds may further be confirmed by the molecular refraction of shonanic acid exhibiting an exaltation of +1.04. This is in accordance with the fact that the conjugation is consistently accompanied by an increase in refractivity.

(1) Mahla and Tiemann, *Ber.*, **33** (1900), 1931.

(2) Thiele, *Ann.*, **308** (1899), 339.

(3) Duden and Lemme, *Ber.*, **35** (1902), 1339.

(4) Straus, *Ber.*, **42** (1909), 2866.

(5) Semmler, *Ber.*, **36** (1903), 1753.

(6) (7) (8) (9) Houben, "Die Methoden der org. Chem.", Vol. II, 971.

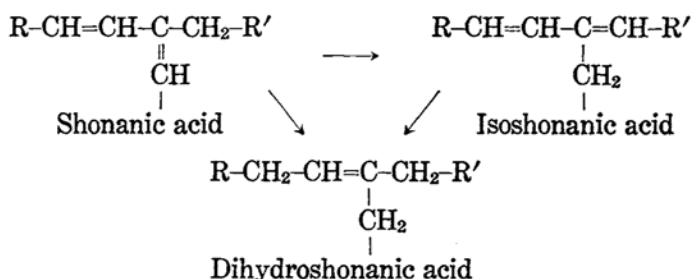
(10) Thiele and Rössner, *Ann.*, **306** (1899), 201.

Shonanic acid is isomerized to isoshonanic acid when heated with strong aqueous sodium hydroxide at about 110°C. Isoshonanic acid has the same formula  $C_{10}H_{14}O_2$  as shonanic acid but melts at 45°C.

Though the melting point of iso-acid is near that of shonanic acid, they are distinctly different. Thus a mixture of both substances shows a depression of the melting point, and isoshonanic amide melts at 107–108° while shonanic amide at 116–117°, and, furthermore, isoshonanic acid can be recrystallized from 60% ethyl alcohol, while shonanic acid cannot.

Isoshonanic acid  $C_{10}H_{14}O_2$ , when reduced with sodium and ethyl alcohol, gives dihydroshonanic acid, while, if reduced catalytically, it absorbs 4 atoms of hydrogen to form tetrahydroshonanic acid. The isomeric change, therefore, should be regarded to be due to the shifting of the double bond and not to the change of ring system nor to the hydration at the double bond as in the cases of methylene-malonic acid<sup>(11)</sup>, crotonic acid<sup>(12)</sup>, linolic acid<sup>(13)</sup>, and acrylic acid<sup>(14)</sup>. And it should also be noted that the isomerized acid boils higher by 13° than the original acid. Y. Fujita<sup>(15)</sup>, who arranged a number of examples of boiling points as regards isomeric substances with double bond at different positions, states that an elevation of 6–12° is observed only in the case of a shifting of the semicyclic double bond into the six-membered ring (table 4 of his report).

The presence of such a semicyclic double bond in the molecule of shonanic acid will be ascertained by further investigations. At any rate the relation between shonanic and isoshonanic acids, as regards their double bonds, may be represented as follows:



Thus to show the relation between shonanic, isoshonanic, dihydroshonanic, and tetrahydroshonanic acids:

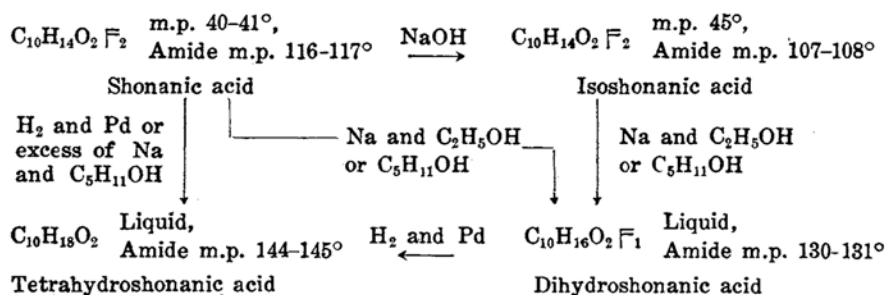
(11) Zelinsky, *Ber.*, **22** (1889), 3302.

(12) Stoemer and Stockmann, *Ber.*, **47** (1914), 1786.

(13) Schicht and Grün, D. R. P. 287660 (1915).

(14) Erlenmeyer, *Ann.*, **191** (1878), 231; Linnemann, *Ber.*, **8** (1875), 1095.

(15) Fujita, *J. Chem. Soc. Japan*, **52** (1931), 210.



### Experimental.

I. **Extraction of Acids and Phenols from the Wood.** The wood chopped into small slices of about  $10 \times 3 \times 15$  cm. in size was extracted with a slight excess of 5% sodium hydroxide solution for 3 days. The alkaline solution was decanted and the sliced wood washed thoroughly with water until reddish brown colour disappeared. The alkaline extract thus obtained was then acidified with dilute sulphuric acid when an insoluble organic matter separated which was extracted with ether and dried over anhydrous sodium sulphate. On distilling off the solvent there remained a tarry substance, which was then subjected to steam distillation to separate the volatile part from resinous matter.

The white, turbid distillate was neutralized with aqueous sodium carbonate and then the solution was concentrated to a smaller bulk and re-acidified to precipitate the acidic substance. The oily substance thus separated was taken in ether and then the ethereal solution was shaken with a solution of sodium bicarbonate to extract the organic acids free from phenolic substances.

This treatment was repeated twice when the yield of acidic and phenolic portions were as follows: wood taken 120 kg., acids 508 g. (0.42%), phenols 18 g. (0.015%). The acidic portion had the following properties:  $d_4^{20}$  1.0450,  $n_D^{20}$  1.4975,  $\alpha_D^{22}$   $-2.8^\circ$ , acid value 306.8.

II. **Isolation of Shonanic Acid.** The acidic substance was fractionated 3 times under diminished pressure with Widmer's fractionating column and the fractions with the properties shown in Table 1 were obtained.

Table 1.

Fr. No.	B.p./6 mm.	$n_D^{20}$	$d_4^{20}$	$\alpha_D^{22}$	Wt. (g.)	Wt. (%)
1	133-134	1.4905	1.0244	$-2.72$	74	14.92
2	134-135	1.4905	1.0233	$-2.72$	97	19.60
3	135-136	1.4912	1.0238	$-3.56$	92	18.55
4	136-137	1.4920	1.0244	$-3.56$	61	12.30
5	137-138	1.4935	1.0264	$-4.20$	36	7.25
6	138-139	1.4950	1.0290	$-4.20$	20	4.03

Table 1. (*Concluded*)

Fr. No.	B.p. /6 mm.	$n_D^{30}$	$d^{30}$	$\alpha_D^{22}$	Wt. (g.)	Wt. (%)
7	139-140	1.4988	1.0320	-5.52	22	4.43
8	140-141	1.5011	1.0373	-5.80	18	3.69
9	141-142	1.5018	1.0371	-6.68	9	1.84
10	142-145	1.5085	1.0445	nil	9	1.84
11	145-148	1.5170	1.0577	-3.80	20	4.03
12	148-149	1.5179	1.0577	nil	11	2.22
13	149-152	1.5205	1.0645	nil	9	1.82
14	152-154/5mm.	1.5205	1.0797	+3.60	12	2.42
Residue					6	1.21

Fractions 1, 2 and 3, on standing at room temperature, deposited a small quantity of crystals and on shaking the vessel the whole of the contents coalesced at once into a crystalline mass. By nucleating fractions 4 and 5 with the crystals, they partly crystallized but fractions 6, 7, 8, and 9 remained liquid, while nearly half of fractions 10 and 11 were found to crystallize. From the residue of distillation some crystalline substance was obtained, the addition of which to fractions 14 and 13 resulted in partial solidification

of both. The crystalline substances were then separated from the fluid ones by filtration (Table 2).

Table 2.

Fractions	Cryst. subst. (g.)	Liquid subst. (g.)
1-4	300	22
5	8	25
6-9	—	69
10-12	28	12
13	2	6
14 and residue	13	—

The crystalline substance from fractions 1-4 and 5 melted at 39-41° after repeated recrystallization from petroleum ether (b.p. 40-50°), while crystals from fractions 10-12 showed a melting point 78-81° after one recrystallization from 60% ethyl alcohol. The crystals from fraction 14 and from the residue were recrystallized twice from 85% ethyl alcohol when it showed a melting point

103°. The liquid portion from 1-4, 5, 6-9, 10-12, and 13 were separately fractionated once again and fractions boiling at 136-138°/6 mm. and 138-141°/6 mm. were obtained.

The former solidified to a crystalline mass melting at 40-41°, while the latter remained liquid. In this way the acidic substance was finally separated into four distinct portions shown in Table 3.

Table 3.

Portions	Wt. (g.)	Acid value	Bromine value	Ag % in Ag-salt	Proposed name
1 (m.p. 40-41°)	325	336.8	960.3	39.52	shonanic acid
2 (b.p. 139-141°/7mm.)	98	332.8	932.2	39.58	—
3 (m.p. 78-81°)	18	336.2	930.8	38.85	—
4 (m.p. 103°)	8	336.2	948.7	38.62	—

III. The Properties of Shonanic acid. Physical properties of the acid: b.p. 264°/754 mm., 134-134.5°/6 mm.; m.p. 40-41°;  $d_4^{25}$  1.016;  $n_D^{25}$  1.4842;  $[\alpha]_D^{25}$  -0.75°; M.R. obs. as  $C_{10}H_{14}O_2$  ( $n^2$ -formula) 47.82, calc. for  $C_{10}H_{14}O_2F_2$  46.78, exallation +1.04; acid value 336.8, calc. for  $C_{10}H_{14}O_2$  337.3;  $[\alpha]_D^{18}$  -0.75° in alcohol (mean of 4 observations). (Found: C, 72.05, 72.40; H, 8.62, 8.47. Calculated for  $C_{10}H_{14}O_2$ : C, 72.3; H, 8.4%.)

The basicity of the acid was determined by the electrolytic conductivity method. The difference of the equivalent conductivities of N/32 and N/1024 sodium salt solutions was found  $10 \times 1.09$ . From the value 1.09 shonanic acid must be monobasic.

The molecular formula was determined by analysis of silver shonanate. The silver salt was prepared in the ordinary way which represented a white amorphous powder. It was dried in vacuo at 100°C. and then a weighed quantity was calcined (Found: Ag, 39.58, 39.55%). The results are in good accord with the supposed molecular formula  $C_{10}H_{14}O_2$  for shonanic acid.

The theoretical values calculated for this formula agree completely with the corresponding experimental data except molecular refraction.

To determine the number of the double bond, 11.008 g. of sample dissolved in 50 c.c. absolute alcohol was catalytically hydrogenated at ordinary temperature with palladium on barium sulphate as catalyser and it was proved that the substance contains two double bonds in its molecule:  $H_2$  gas absorbed, 3385 c.c. (30°C. 753.3 mm.) or 2895 c.c. (0°C., 760 mm.); calc. for  $C_{10}H_{14}O_2F_2$ , 2970 c.c. (0°C., 769 mm.). Sample (0.2157 g.) absorbed 0.2019 g. bromine, while  $C_{10}H_{14}O_2F_2$  requires 0.4158 g. The amount of bromine absorbed corresponds to 1/2 of the theoretical, namely the acid absorbed only 2 atoms of bromine.

IV. Some Derivatives of Shonanic Acid. (1) *Acid Chloride*. The acid chloride was prepared as usual by heating a mixture of the acid and phosphorous trichloride. The product obtained was a colourless mobile fluid with a characteristic odour. The physical properties were as follows: b.p. 106-107°/20 mm., 215°/760 mm.;  $d_4^{20}$  1.0577;  $n_D^{20}$  1.4955.

(2) *Amide*. The amide was prepared by adding the acid chloride to cold concentrated aqueous ammonia. The amide obtained was collected, washed with cold water, and recrystallized from 50% ethyl alcohol. It melted at 116-117°C. By adding water to the filtrate another crop of the amide was obtained. (Found: N, 8.44, 8.32. Calc. for  $C_{10}H_{15}ON$ : N, 8.48%.)

(3) *Anilide*. The anilide was obtained by the interaction of aniline and the acid chloride in the cold. It melted at 111–112° after a recrystallization from 60% methyl alcohol. By further purification the melting point was not raised. (Found: N, 5.70. Calc. for  $C_{10}H_{19}ON$ : N, 5.8%.)

(4) *Methyl Ester*. The methyl ester was obtained by gentle heating of a mixture of methyl alcohol and the acid chloride on the water bath. The reaction product was poured into water when an oily substance separated out which was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and then ether was distilled off. The remainder distilled at 113–114° under 20 mm. and showed the following properties: b.p. 222°/760 mm., 113–114°/20 mm.;  $n_D^{20}$  1.4758;  $d_4^{20}$  0.9848;  $\alpha_D^{28}$  –2.84°; sap. value 313.1, calc. for  $C_{11}H_{16}O_2$  311.1.

(5) *Ethyl Ester*. The ethyl ester was prepared by heating a mixture of the acid (10 g.) with an excess of absolute alcohol containing 2.5% HCl on the boiling water bath for an hour. The reaction product, after distilling off the excess of ethyl alcohol, was dissolved in ether and the ethereal solution was shaken with water and sodium bicarbonate solution in order to remove traces of alcohol and acidic substances present and then fractionally distilled under diminished pressure. The amount of ethyl ester obtained was 9.3 g.; b.p. 228–229°/759 mm., 106–108°/7 mm.;  $d_4^{20}$  0.9568;  $n_D^{20}$  1.4674;  $\alpha_D^{18}$  –4.24°; bromine value, 0.2739 g. absorbs 0.221 g. of bromine,  $C_{12}H_{18}O_2$  requires 0.225 g.

(6) *Dihydroshonanic Acid*. Shonanic acid (15 g.) was dissolved in 150 c.c. of ethyl alcohol and 10 g. of metallic sodium (2.5 times of the theoretical amount) was added in small portions. The acidic product was isolated from the reaction product in the usual way and then distilled under reduced pressure. The rectified product showed the following properties: b.p. 142–143.5°/7 mm.;  $d_4^{20}$  1.0333;  $n_D^{20}$  1.4985; M.R. obs. 47.69, calc. for  $C_{10}H_{16}O_2$   $F_1$  47.35; bromine value 879 (0.1131 g. absorbs 0.0995 g. of bromine), calc. for  $C_{10}H_{16}O_2$   $F_1$  952. (Found: C, 71.47, 71.17; H, 9.31, 9.56. Calculated for  $C_{10}H_{16}O_2$ : C, 71.4; H, 9.5%, Analysis of the silver salt: Ag, 39.24, 39.37. Calculated for  $C_{10}H_{15}O_2Ag$ : Ag, 39.24%.)

The amide prepared by the interaction of aqueous ammonia and the acid chloride (b.p. 58.5°/16 mm., prepared as usual by using 1 g.  $PCl_3$  for 1 g. acid) melted at 121–128° without any purification. The purified amide after twofold recrystallization from 20% ethyl alcohol, melted at 129–130°C.

(7) *Catalytic Hydrogenation of Dihydroshonanic Acid*. In order to determine the number of double bonds in the molecule of dihydroshonanic acid, it was hydrogenated catalytically with hydrogen and palladium and it was found to contain only one double bond: 2.32 g. of substance absorbed 359.0 c.c. (28°C., 758.0 mm.) or 312.6 c.c. (0°C., 760 mm.) of  $H_2$ .  $C_{10}H_{16}O_2$   $F_2$  requires 309.3 c.c. Physical properties of the hydrogenated acid (tetrahydroshonanic acid): b.p. 142–143°/7 mm.;  $d_4^{20}$  0.9929;  $n_D^{20}$  1.4704; M.R. obs. 47.73, calc. for  $C_{10}H_{18}O_2$  47.72; bromine value nil.

The amide was prepared from the acid chloride (b.p. 117°/20 mm.) and aqueous ammonia. It melted at 144°C. after one recrystallization from 60% ethyl alcohol and was proved to be identical by melting in admixture with the amide of tetrahydroshonanic acid obtained by catalytic hydrogenation of shonanic acid (see below).

(8) *Catalytic Reduction of Shonanic Acid*. Tetrahydroshonanic acid, the saturated acid, obtained by hydrogenation of shonanic acid with hydrogen and palladium on barium

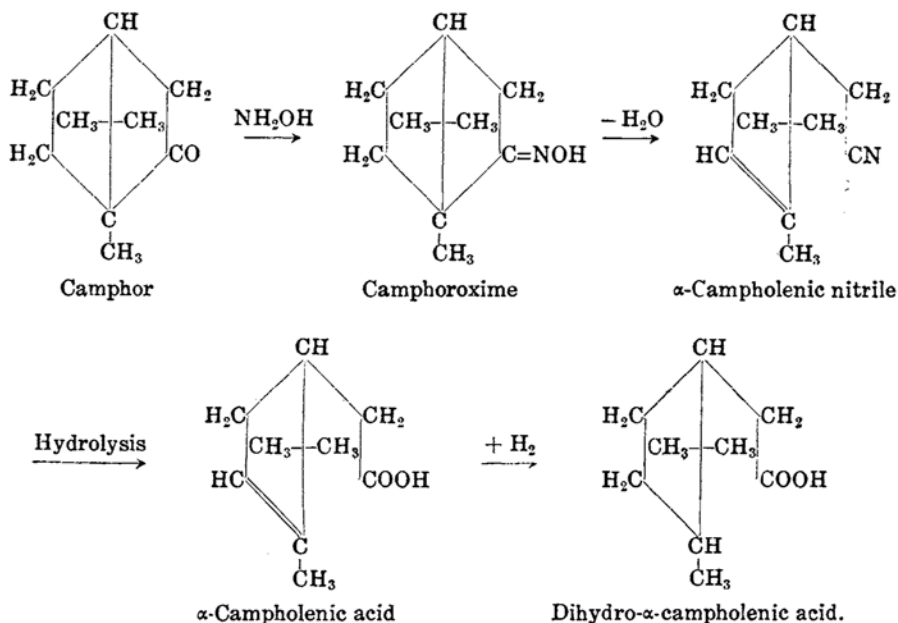
sulphate showed the properties: b.p. 140–141°/8 mm.;  $d_4^{27}$  0.9950;  $n_D^{27}$  1.4690; M.R. obs. 47.58, calc. for  $C_{10}H_{18}O_2$  47.72; bromine value nil. Analysis of the silver salt: Ag, 39.00. 39.02. Calculated for  $C_{10}H_{17}O_2Ag$ : 38.96%.

The acid was resistant against dilute permanganate solution in the cold showing that the substance was a saturated acid; this may also be recognized by the fact that the bromine value of the acid was proved to be nil as already mentioned.

The acid chloride prepared as usual by warming a mixture of the acid and phosphorous trichloride had the following properties: b.p. 115°/19 mm.;  $d_4^{30}$  1.014;  $n_D^{30}$  1.4704; M.R. obs. 51.64, calc. for  $C_{10}H_{17}OCl$  51.05.

The amide prepared from the acid chloride and aqueous ammonia was plates with pearly lustre and melted at 143° after once recrystallized from ethyl alcohol (Found: N, 8.31. Calculated for  $C_{10}H_{19}ON$ : N, 8.28%).

Among the known acids of formula  $C_{10}H_{18}O_2$ , we find dihydro- $\alpha$ -campholenic acid, the amide of which melts at 143–144°C. In order to ascertain whether or not tetrahydroshonanic acid is identical with dihydro- $\alpha$ -campholenic acid, the latter was prepared from camphor as shown below:



Camphoroxime was prepared according to the method described by Auwers<sup>(16)</sup>, m.p. 118–120°.  $\alpha$ -Campholenic nitrile was prepared by dehydration of camphoroxime with 25%  $H_2SO_4$ <sup>(17)</sup>. The product being the mixture of  $\alpha$ - and  $\beta$ -campholenic nitriles, was fractionally distilled 3 times under reduced pressure and the two following main fractions were obtained. Fraction 1: b.p. 220–225°;  $d_4^{30}$  0.9063;  $n_D^{30}$  1.4700; yield 20% of the product

(16) Auwers, *Ber.*, **22** (1889), 605.

(17) Tiemann, *Ber.*, **28** (1895), 1083.



(Found: N, 9.60. Calc. for  $C_{10}H_{15}ON$ : N, 9.4%). Fraction 2: b.p. 225–227°;  $d_4^{30}$  0.9122;  $n_D^{30}$  1.4648; yield 60% of the product (Found: N, 9.51. Calc. for  $C_{10}H_{15}ON$ : N, 9.4%).

Fraction 1 was found to represent  $\beta$ -campholenic nitrile by preparing  $\beta$ -campholenic amide melting at 84–86.5°<sup>(18)</sup>. The amide from fraction 2 showed melting point 124–125° agreeing with that of  $\alpha$ -campholenic amide (m.p. 125°)<sup>(19)</sup>,  $[\alpha]_D^{25} = -3.6^\circ$ .

Fraction 2 was treated according to Wallach<sup>(20)</sup> with an excess of alcoholic potash and the product was fractionally distilled under ordinary pressure. Fraction (1): b.p. 224–249°;  $d_4^{30}$  0.9766;  $n_D^{30}$  1.4606; yield 18%. Fraction (2): b.p. 253–255°;  $d_4^{30}$  0.9973;  $n_D^{30}$  1.4664; yield 68%. The boiling point, density, and refractive index of fraction (2) correspond with those of  $\alpha$ -campholenic acid (b.p. 256°,  $d$  0.9920,  $n_D$  1.4712)<sup>(21)</sup> (Found: C, 71.23; H, 9.62. Calculated for  $C_{10}H_{16}O_2$ : C, 71.4; H, 9.5%). Although fraction (1) had the boiling point of  $\beta$ -campholenic acid (b.p. 247–248°), it showed no tendency of solidification probably owing to the presence of impurity such as campholene, the by-product produced by distillation of  $\alpha$ - and  $\beta$ -campholenic acids.

Fraction (2) was dissolved in absolute alcohol, and hydrogenated catalytically with hydrogen and palladium on barium sulphate. 10.10 g. absorbed 1528 c.c. (30°, 753.6 mm.) or 1308 c.c. (0°, 760 mm.)  $H_2$ .  $C_{10}H_{16}O_2$   $\bar{F}_1$  requires 1348 c.c.

The acid here obtained, being saturated, does not absorb bromine and is stable to permanganate in the cold. The properties of the product were as follows: b.p. 259–261°/762 mm., 154–155°/19 mm.;  $d_4^{27}$  0.9736;  $n_D^{27}$  1.4578;  $\alpha_D^{27} +10.75^\circ$ ; acid value 331.0. Analysis of the silver salt: Ag, 38.94. Calc. for  $C_{10}H_{17}O_2Ag$ : 38.96%. The amide prepared from this acid in the usual way showed melting point 143–145°. On examining the melting point of a mixture of amides of tetrahydroshonanic and dihydro- $\alpha$ -campholenic acids, it softened at about 118° and melted at 139°, showing a depression of 6°. Thus it follows that they should be quite different substances. Tetrahydroshonanic acid ( $C_{10}H_{18}O_2$ ), therefore, is a new substance.

**V. Preparation of Isoshonanic Acid.** Shonanic acid (5 g.) and 20 g. of 50% NaOH solution were heated to gentle boiling for about 4 hours, and then the product was fractionated under reduced pressure. The fraction distilling at 151–152°/7 mm. (b.p. 277–278°/756 mm.) solidified on cooling, and after recrystallization from 60% ethyl alcohol the substance melted at 45–46°, and in admixture with shonanic acid (m.p. 40–41°) melted at once, showing that they are quite different substances. Other evidence supporting this view are: shonanic acid cannot be recrystallized from 60% ethyl alcohol while isoshonanic acid can be, and that the melting points of the amides are different, viz. 117° and 107°. Found: bromine value, 957. Calc. for  $C_{10}H_{14}O_2$   $\bar{F}_2$ : 963. Found: acid value, 335. Calc. for  $C_{10}H_{14}O_2$ : 337. Analysis of the silver salt: Ag, 39.41. Calc. for  $C_{10}H_{13}O_2Ag$ : Ag, 39.53%.

**Acid Chloride.** Obtained from 2 g. of the acid and 1.6 g. of  $PCl_3$ . B.p. 107–108°/20 mm.  $n_D^{19}$  1.5077.

(18) Tiemann, *Ber.*, **30** (1897), 245.

(19) Nägeli, *Ber.*, **17** (1884), 2071.

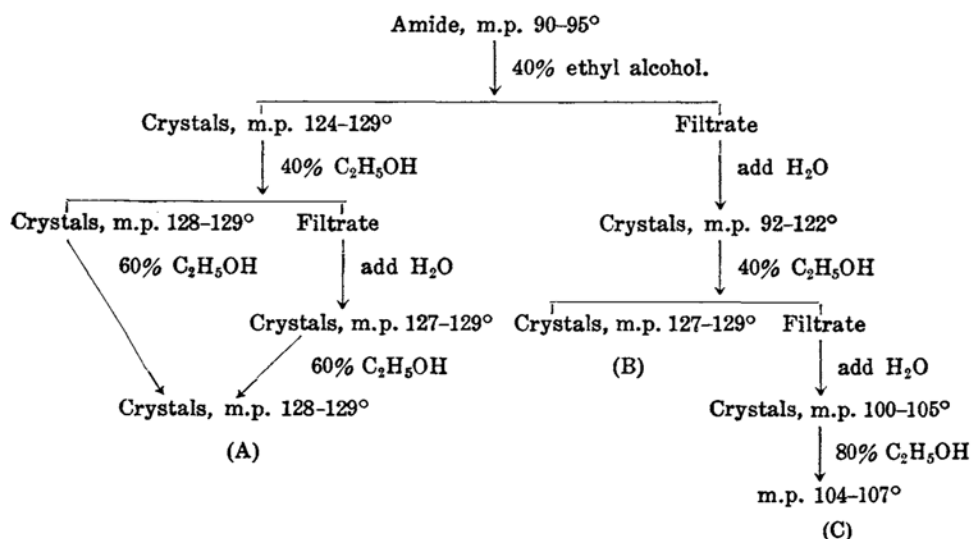
(20) Wallach, *Ann.*, 269 (1892), 336.

(21) Wallach, *Ann.*, **269** (1892), 338.

*Amide.* Prepared from acid chloride and aqueous ammonia. It melted at 102–106° without any purification, and at 107–108° after recrystallization from alcohol, the melting point rising no more on further purification. A mixture of shonanic amide (m.p. 116–117°) and this amide melted at 88–98°, showing that they are quite different substances.

VI. Preparation of Dihydroshonanic Acid from Isoshonanic Acid. Isoshonanic acid (3 g.) was dissolved in 100 c.c. of ethyl alcohol and reduced with 3 g. of metallic sodium. The product obtained showed the following properties: b.p. 144–148°/8 mm.;  $d_4^{20}$  1.0290;  $n_D^{20}$  1.4980; M.R. obs. 47.86, calc. for  $C_{10}H_{16}O_2$   $F_1$  47.35; bromine value 943 (0.1379 g. absorbs 0.1300 g. Br), calc. for  $C_{10}H_{16}O_2$   $F_1$  952.

*Amide.* The amide prepared from the acid chloride (b.p. 114/21 mm.,  $d_4^{20}$  1.0547,  $n_D^{20}$  1.5002) and aqueous ammonia, melted at 90–95°, which was fractionally recrystallized as follows:



Crystals (A) and (B) were found to be dihydroshonanic amide by examination of the melting points of various mixtures, while crystals (C) was proved to be crude isoshonanic amide.

### Summary.

(1) The existence of an unknown acid in the volatile part from the wood of *Libocedrus formosana*, Florin, or "Shōnan-Boku" is reported.

(2) Shonanic acid is an unsaturated monobasic acid with a monocyclic structure of the formula  $C_{10}H_{14}O_2$ , melting at 40–41°. Its amide melts at 116–117° and the anilide at 111–112°.

(3) Shonanic acid can be converted into tetrahydroshonanic acid by absorption of four atoms of hydrogen when reduced catalytically, while it absorbs only two atoms of bromine, and when reduced with sodium and ethyl alcohol an unsaturated acid, viz. dihydroshonanic acid ( $C_{10}H_{16}O_2$ ), is obtained. These experimental facts together with the fact that the molecular refraction of shonanic acid exhibits an eminent exaltation lead to the conclusion that conjugated double bonds exist in its molecule.

(4) Though tetrahydroshonanic amide melts at  $144^\circ$ , it was proved that the acid is quite different from dihydro- $\alpha$ -campholenic acid ( $C_{10}H_{18}O_2$ , amide m.p.  $144^\circ$ ).

(5) Shonanic acid isomerizes to isoshonanic acid by the action of hot strong alkali solution. Iso-acid melts at  $45^\circ$  and gives an amide melting at  $107-108^\circ$ .

(6) The isomerisation of shonanic acid to isoshonanic acid is accompanied by the elevation of the boiling point to the extent of  $13^\circ C$ . This phenomenon may probably be due to the migration of semicyclic double bond into the ring system of the acid, which must be ascertained by further investigations.

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