Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. II. On the Reduction and Bromination of Shonanic Acid.

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In a previous communication[1] the author has reported the presence of a new acid (shonanic acid) among the volatile acidic ingredients of the wood of *Libocedrus formosana*, Florin, or "Shônan-Boku" and the general properties of the acid. The present communication deals with its reduction, the addition of bromine and some derivatives derived from the bromination product.

The behaviour of shonanic acid toward reducing agents is rather delicate and complicated. If shonanic acid be reduced with sodium and ethyl alcohol the product consists of about 92% of dihydroshonanic acid $C_{10}H_{16}O_2$ 「1 and 8% of tetrahydroshonanic acid $C_{10}H_{18}O_2$ (saturated acid), while if amyl alcohol be used instead of ethyl alcohol, about 75% dihydroshonanic and 25% tetrahydroshonanic acids resulted. In the latter case by using 20 times the theoretical amount of sodium necessary for the production of dihydro-acid, nearly all of the acid was converted into the tetrahydro-acid. With sodium amalgam dihydroshonanic acid can not be reduced any further, and with sodium and ethyl alcohol a very small portion of the acid is reduced to the tetrahydroshonanic acid, while in case of using excess of metallic sodium and amyl alcohol the reduction proceeds steadily until nearly all of the acid (dihydro-acid) is converted into the tetrahydro-acid.

(1) This Bulletin, **11** (1936), 759.

The reason why shonanic acid, which contains two conjugated double bonds, produces the saturated acid when reduced with amyl alcohol and large amount of sodium, may be explained as follows:—

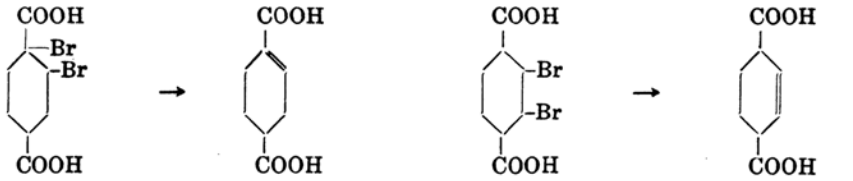
The reduction product of the first step, namely dihydroshonanic acid, may be isomerized to readily reducible α,β-unsaturated acid as in the case of $\Delta^{2,5}$-dihydroterephthalic[2] or of $\Delta^{1,3}$-dihydroterephthalic[3] acids by the action of amyl alcoholate at tolerable high temperature and the isomerized acids thus formed will be transformed into the saturated acid by further action of sodium and amyl alcohol.

On adding bromine to a solution of shonanic acid in ether, glacial acetic acid or carbon tetrachloride, two atoms of bromine will be taken up by the acid. The product, namely shonanic acid dibromide $C_{10}H_{14}O_2Br_2$, is a viscous liquid with a pale yellowish tint. It is unstable against permanganate solution even in cold but does not admit any further addition of bromine. Shonanic acid dibromide is soluble in alkaline solution and when treated with zinc dust in hot glacial acetic acid shonanic acid is regenerated with expulsion of bromine. From this fact it should be anticipated that the addition of two bromine atoms takes place at 1,2 or 3,4-position of the conjugated system. There are three modes of addition of bromine atom to the conjugated system as shown in the following:—

$$\text{R-CH=CH-CH=CH-R}' \xrightarrow{+2\text{Br}} \begin{cases} \text{R-CHBr-CHBr-CH=CH-R}' & \text{(A)} \\ \text{R-CH=CH-CHBr-CHBr-R}' & \text{(B)} \\ \text{R-CHBr-CH=CH-CHBr-R}' & \text{(C)} \end{cases}$$

In the case of (A) or (B) bromine atoms are taken away by zinc as to produce double bond, while in the case of (C) bromine atoms are substituted by hydrogen atoms. The examples of these reactions are shown in the following scheme:—

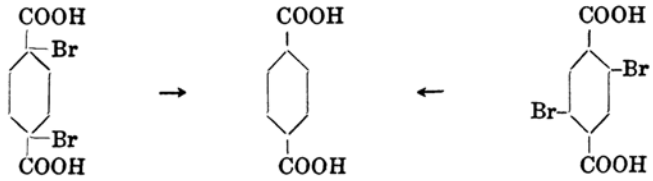
Example of the case of (A) or (B).[4]



Δ^1-Tetrahydroterephthalic acid dibromide — Δ^1-Tetrahydroterephthalic acid — Δ^2-Tetrahydroterephthalic acid dibromide — Δ^2-Tetrahydroterephthalic acid

(2) Baeyer, *Ann.*, **251** (1889), 281, 290, 306.
(3) Baeyer, *Ann.*, **269** (1892), 189.
(4) Baeyer, *Ann.*, **245** (1889), 169; Baeyer and Herb, *Ann.*, **258** (1890), 38.

Example of the case of (C).[5]



1,4-Dibromo-hexahydro-terephthalic acid — Hexahydro-terephthalic acid — 2,5-Dibromo-hexahydro-terephthalic acid

Following these examples, the addition of bromine to shonanic acid should represent the case of (A) or (B), and in the literature we find examples of this mode of addition in cases of sorbic acid[6] and cynnamylidene acetic acid.[7]

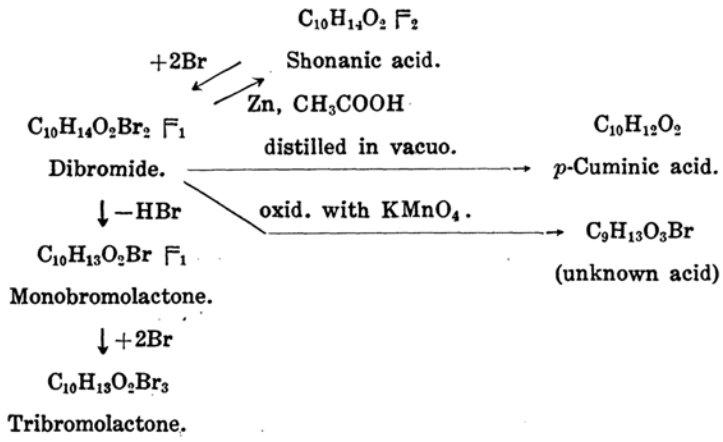
When shonanic acid dibromide is distilled in vacuo it decomposes to give *p*-cuminic acid. This formation of *p*-cuminic acid, however, must not be taken as the proof of the presence of isopropyl group in the molecule of shonanic acid, as shonanic acid as well as dihydroshonanyl alcohol on oxidation with permanganate give dimethylmalonic or dimethylglutaric acids, and no derivatives containing isopropyl group were obtained, the detailed description of which will be reported in the next communication.

Shonanic acid dibromide, on the other hand, on standing at ordinary temperature gradually turns into monobromolactone $C_{10}H_{13}O_2Br$ by giving off one mol of HBr. The substance is no more soluble in alkali but absorbs two more bromine atoms to give rise to a crystalline tribromolactone $C_{10}H_{13}O_2Br_3$, melting at 212° (with decomp.). The monobromolactone seems to be a γ-lactone from its mode of formation as analogous in cases of diallylmalonic,[8] phenylallylacetic,[9] or aticonic acids:[10] these substances add bromine to give dibromides and then giving off HBr gas form γ-lactones. A large number of experiments about the formation of lactones from Δ^{β}-, Δ^{γ}- and Δ^{α}-acids in which addition of bromine accompanied by fission of one mol of HBr are reported by J. Bougault,[11] by whom it was ascertained that Δ^{β}- and Δ^{γ}-acids give γ-lactones in these cases.

(5) Baeyer, *Ann.*, **245** (1889), 176, 151.
(6) Auwers and Heyna, *Ann.*, **434** (1923), 140.
(7) Auwers and Müller, *Ann.*, **434** (1923), 165.
(8) Hjelt, *Ann.*, **216** (1882), 61.
(9) Wislicenus and Goldstein, *Ber.*, **29** (1896), 2601.
(10) Fittig, *Ann.*, **304** (1899), 133.
(11) Bougault, *Compt. rend.*, **139** (1904), 864; **143** (1906), 398; **146** (1906), 140.

On oxidation with alkaline permanganate shonanic acid dibromide gives a crystalline bromo-acid $C_9H_{13}O_3Br$ (m.p. 239° with decomp.), the nature of which is not yet clear.

The following scheme shows the various changes mentioned above:



Experimental.

I. Action of reducing agents on shonanic acid. (1) *Action of sodium amalgam.* 10 g. of shonanic acid was dissolved in sodium bicarbonate solution and 300 g. of sodium amalgam (2.5%) was added with constant stirring and cooling while CO_2 gas was introduced into the reaction mixture in order to neutralize NaOH set free during the course of the reaction. After all the sodium amalgam has been consumed, the alkaline solution was acidified with dilute sulphuric acid when an organic acid made appearance which was collected with ether. After removal of the solvent the residue was fractionally distilled under diminished pressure and it was found that almost whole of the substance distilled at 134–135° under 6 mm. The distillate solidified to a compact mass on standing in cold, which melted at 40° after one recrystallization from light petroleum ether. The amide prepared therefrom melted at 116–117° and showed no depression of the melting point when mixed with shonanic amide. (Analysis of the silver salt: Ag, 39.55. Calculated for $C_{10}H_{13}O_2Ag$: Ag, 39.53%.)

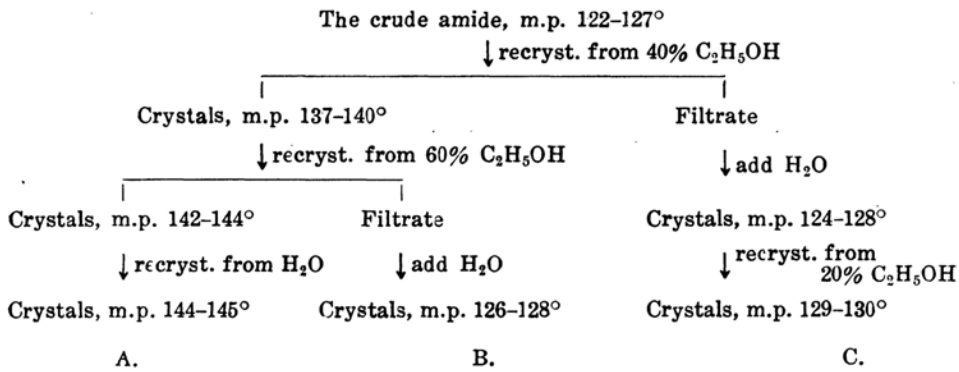
Thus it was shown that the reduction of shonanic acid can not be achieved by sodium amalgam as in the case of dihydro-*p*-xylic acid. The author, therefore, made a trial to obtain dihydro-acid $C_{10}H_{16}O_2$ F1 from shonanic acid by means of sodium and amyl alcohol, as by this treatment the above-mentioned dihydro-*p*-xylic acid gives tetrahydro-*p*-xylic acid.

(2) *Reduction with sodium and amyl alcohol.* 5 g. of shonanic acid was dissolved in 100 c.c. of amyl alcohol and 3.5 g. of metallic sodium (2.5 times of the theoretical amount necessary to produce $C_{10}H_{16}O_2$ F1 from $C_{10}H_{14}O_2$ F2) was added in small portions, heating the mixture, and adding water (about 2–3 c.c. at a time)

from time to time in order to ensure the complete dissolution of the metallic sodium. After all the sodium has been taken up, the reaction product was poured into water and the aqueous layer separated and shaken thoroughly with ether to remove traces of amyl alcohol. The alkaline solution was then acidified with dilute sulphuric acid and the organic acid set free was extracted with ether. The extract, after evaporating the excess of the solvent, was rectified under reduced pressure. B.p. 146–147°/9 mm.; d_4^{20} 1.0217; n_D^{20} 1.4892; M.R. obs. 47.48, calculated for $C_{10}H_{16}O_2$ F_1 47.35; bromine value 711 (0.1365 g. absorbed 0.097 g. of bromine), calculated for $C_{10}H_{16}O_2$ F_1 952.

The difference between the theoretical and the experimental bromine values may be attributed to the presence of the saturated acid (tetrahydroshonanic acid, $C_{10}H_{18}O_2$) and this conjecture was proved correct by the fact that tetrahydroshonanic amide was actually obtained from the reduction product. The ratio of saturated and unsaturated acid can roughly be calculated from the theoretical and experimental bromine values as follows: saturated acid 74.6, unsaturated acid 25.4%. (Found: C, 71.04, 70.96; H, 10.13, 10.06. Calculated for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5; $C_{10}H_{18}O_2$: C, 70.6; H, 10.6%. Analysis of the silver salt: Ag, 39.27. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride was prepared from the acid (1 g.) and phosphorus trichloride as usual and it was added to cold aqueous ammonia to obtain the amide. The amide melted at 122–127°, which was subjected to fractional recrystallization as shown below:



Crystals A were proved to be identical with tetrahydroshonanic amide prepared from saturated acid (tetrahydro-acid) obtained by catalytic reduction of shonanic acid; crystals B might have been crude mixture of A and C, but on account of the scarcity of the substance further purification was not carried out; crystals C represented dihydroshonanic amide whose melting point remained constant on further purifications. (Found: N, 8.56. Calculated for $C_{10}H_{17}ON$: N, 8.4%.) Other evidences for the presence of the saturated acid therein may also be recognized among the experimental data observed in the analysis of the silver salt, elementary analysis and bromine value.

(3) *Reduction with a large amount of sodium and amyl alcohol.* 10 g. of the acid dissolved in 300 c.c. of amyl alcohol was kept hot on a boiling water-bath and 30 g. of sodium was added in small portions with vigorous stirring. 2–5 c.c. of water was added several times during the course of the reaction in order to promote the reaction. The reaction product was poured into water, stirred vigorously for 10 minutes and the alkaline layer was separated. The alkaline solution was acidified and the organic acid set free was extracted with ether. The extract after removal of the solvent was subjected to fractional distillation under reduced pressure. At the beginning of the distillation isovaleric acid, produced as by-product,[12] distilled and then the main fraction boiling at 143–144°/9 mm. came over. The distillate was rectified once more and thus an acid with the following properties was obtained: b.p. 140–141°/8 mm.; d^{30} 0.9863; n_D^{30} 1.4665; M.R. obs. 47.78, calculated for $C_{10}H_{18}O_2$ 47.72; acid value 336.4 (0.5238 g. required 32.11 c.c. of 0.098 N NaOH), calculated for $C_{10}H_{18}O_2$ 329.4; bromine value nil. (Found: C, 70.44, 70.42; H, 10.61, 10.60. Calculated for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58%. Analysis of the silver salt: Ag, 38.90. Calculated for $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Contrary to the previous case the product was an entirely saturated acid (tetrahydroshonanic acid) the amide showing the same melting point as tetrahydroshonanic amide.

Acid chloride. The acid chloride was prepared in the usual manner from 3 g. each of the acid and phosphorus trichloride. Its properties were as follows: b.p. 115–116°/20 mm.; d_4^{30} 1.016; n_D^{30} 1.4713.

Amide. The amide was obtained by the interaction of the acid chloride and aqueous ammonia in plate crystals with pearly lustre, which melted at 143–144° after a crystallization from 50% ethyl alcohol. (Found: N, 8.23. Calculated for $C_{10}H_{19}ON$: N, 8.28%.)

II. Action of reducing agents on dihydroshonanic acid. (1) *Catalytic hydrogenation of dihydroshonanic acid.* As already stated in the previous communication, it was found that dihydroshonanic acid absorbs two atoms of hydrogen to give tetrahydroshonanic acid $C_{10}H_{18}O_2$.

(2) *Action of sodium amalgam.* 5 g. of dihydroshonanic acid (containing ca. 92% of dihydroshonanic acid obtained by the experiment IV-(6) in the previous communication) was dissolved in an excess of 10% sodium hydroxide solution and was treated with 400 g. of sodium amalgam (2.5%) (6 times the calculated amount to give $C_{10}H_{18}O_2$) at ordinary temperature with vigorous stirring. The product showed the following properties: b.p. 143–144°/7 mm.; d_4^{30} 1.0328; n_D^{30} 1.4987; M.R. obs. 47.74, calculated for $C_{10}H_{16}O_2$ $\digamma_1$ 47.35; bromine value 885 (0.1922 g. absorbed 0.1698 g. of bromine), calculated for $C_{10}H_{16}O_2$ $\digamma_1$ 952.

That the unsaturated acid remains practically unchanged is clear from the bromine value, which tells that dihydroshonanic acid is not at all affected by sodium amalgam.

Amide. The amide was prepared from the acid chloride and aqueous ammonia which melted at 129–130° and was proved to be identical with dihydroshonanic amide

(12) Dumas and Stas, *Ann.*, **35** (1840), 143.

by melting in admixture with that obtained in the experiment IV-(6) (previous communication[1]).

(3) *Reduction with sodium and ethyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of ethyl alcohol and 3.5 g. of sodium (3 times of the theoretical amount of sodium necessary to produce $C_{10}H_{18}O_2$ from $C_{10}H_{16}O_2F_1$) was added in small portions. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 1.0298; n_D^{30} 1.4966; M.R. obs. 47.71, calculated for $C_{10}H_{16}O_2F_1$ 47.35; bromine value 875 (0.1108 g. absorbed 0.0906 g. of bromine), calculated for $C_{10}H_{16}O_2F_1$ 952.

The amount of the saturated acid calculated from the bromine value is ca. 15% showing an increase of the saturated acid by 7% as compared with the starting substance.

Amide. The amide prepared as usual from the acid chloride and aqueous ammonia melted at 107–120° without any purification, which was then subjected to fractional recrystallization as follows:—

The crude amide, m.p. 107–120°
↓ recryst. from 40% C_2H_5OH

Crystals, m.p. 123–133°
↓ recryst. from 60% C_2H_5OH

Crystals, m.p. 140–144°
↓ recryst. from 60% C_2H_5OH
Crystals, m.p. 142–145°
A.

Crystals from the filtrate, m.p. 124–127°
↓ recryst. from 20% C_2H_5OH
Crystals, m.p. 127–129°
↓ recryst. from H_2O
Crystals, m.p. 129°
B.

Crystals from the filtrate, m.p. 118–124°
↓ recryst. from 20% C_2H_5OH
Crystals, m.p. 126–129°
↓ recryst. from H_2O
Crystals, m.p. 128–129°
C.

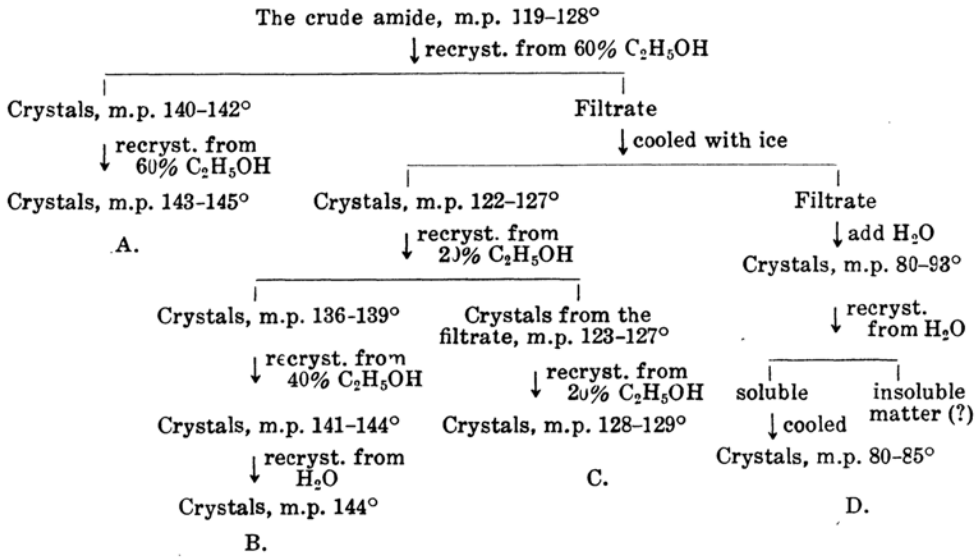
Owing to the scarcity of the material crystals A were without further purification mixed with tetrahydroshonanic amide and the melting point examined. They melted at 142–144°, from which it is obvious that this substance is tetrahydroshonanic amide. Crystals B and C were identified as dihydroshonanic amide in like manner.

(4) *Reduction with sodium and amyl alcohol.* 3 g. of dihydroshonanic acid (preparation of the experiment IV-(6) of the previous report, containing 92% dihydro-acid) was dissolved in 100 c.c. of amyl alcohol and was reduced with 3.5 g. of sodium. The product had the following properties: b.p. 142–144°/7 mm.; d_4^{30} 1.0160; n_D^{30} 1.4870; bromine value 378 (0.1635 g. absorbed 0.0616 g. of bromine), calculated for $C_{10}H_{16}O_2F_1$ 952.

The approximate amount of the saturated acid in the reaction product is about 60% as calculated from the bromine value. (Analysis of the silver salt: Ag, 39.03. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride obtained from 1.3 g. of the acid and 1.5 g. of phosphorus trichloride was treated with aqueous ammonia, and the crude amide

thus obtained melted at 119–128° without any purification, which was fractionally recrystallized as follows.



The crystals A and B were found to be identical with tetrahydroshonanic amide by observing the melting point of mixtures, while the crystals C were found to be identical with dihydroshonanic amide. The crystals D were not further purified as the quantity available became scarce but it can not be considered as crude crystals of C as the former is readily soluble in water while the latter is not.

(5) *Reduction with a large amount of sodium and amyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of amyl alcohol and was treated with 10 g. of sodium as usual. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 0.9930; n_D^{30} 1.4703; M.R. obs. 47.74, calculated for $C_{10}H_{18}O_2$ 47.72; bromine value 26 (0.1472 g. absorbed 0.0038 g. of bromine).

The percentage of the saturated acid therein was found to be about 97%.

Amide. The amide was prepared from the acid chloride (prepared from 2 g. of the acid and 3 g. of phosphorus trichloride) and aqueous ammonia. It melted at 144° after one recrystallization from 60% ethyl alcohol and was found to be identical with tetrahydroshonanic amide obtained by catalytic hydrogenation of shonanic acid.

III. Some derivatives of shonanic acid containing bromine. (1) *Shonanic acid dibromide.* To a well-cooled solution of shonanic acid (acid 10 g. in ether 100 c.c.) 10 g. of bromine was added drop by drop with constant shaking. The colour of the ethereal solution acquired yellowish tint and on removal of the solvent under diminished pressure there remained a colourless viscous oily substance, which showed no tendency of solidification even kept at −5° for several days. The dibromide thus obtained does not admit further addition of bromine whereas it is easily acted on by dilute permanganate solution at 0°. On standing at the ordinary temperature

a portion of the dibromide was gradually converted into grayish monobromolactone (see below).

The dibromide could not be distilled without decomposition and the physical properties of the crude preparation were as follows: d_4^{30} 1.603; n_D^{30} 1.5330; M.R. obs. 63.10, calculated for $C_{10}H_{14}O_2Br_2$ 𝔽$_1$ 62.78. (Found: C, 37.27; H, 4.35; Br, 48.78. Calculated for $C_{10}H_{14}O_2Br_2$: C, 36.81; H, 4.29; Br, 49.06%.)

(2) *Regeneration of shonanic acid from its dibromide.* 10 g. of shonanic acid dibromide freshly prepared as above was dissolved in 60 c.c. of glacial acetic acid, kept cool with the freezing mixture and 50 g. of zinc dust was added in small portions. After all zink dust has been added the reaction mixture was then warmed on a boiling water-bath for an hour. It was then poured into water and the oily acidic substance separated was extracted with ether. The ethereal solution was washed with water to remove acetic acid present, dried over anhydrous sodium sulphate and the ether was distilled off. The reddish brown substance remaining behind was fractionally distilled under reduced pressure, when 3.8 g. of acidic substance came over at 140°/7 mm. It contained no bromine at all, as it gave no Beilstein's flame reaction. The amide prepared from the acid chloride (b.p. 98°/12 mm.) of the substance and aqueous ammonia melted at 116–117° after recrystallization from 50% ethyl alcohol, it was identical with shonanic amide. Thus, by the action of zinc and glacial acetic acid, shonanic acid was regenerated from its dibromide.

(3) *The formation of monobromolactone from the dibromide.* 6.5 g. of shonanic acid dibromide was placed in a round flask and warmed on the water-bath at 40–50° for 4 hours under 40–50 mm. It was then dissolved in ether and by shaking with dilute sodium carbonate solution the unchanged acid was removed. From the ethereal solution a substance with the following properties was obtained (Yield 2.4 g.): d_4^{30} 1.4540; n_D^{20} 1.544; M.R. obs. 53.21, calculated for $C_{10}H_{13}O_2Br$ 𝔽$_1$ 52.81.

The substance is insoluble in alkaline solution, unstable against permanganate and absorbs bromine in cold, showing the substance to be unsaturated. The substance could not be distilled without decomposition. Bromine value 644.6 (0.7983 g. absorbed 0.5146 g. of bromine), calculated for $C_{10}H_{13}O_2Br$ 𝔽$_1$ 653.1. (Found: Br, 32.68. Calculated for $C_{10}H_{13}O_2Br$: Br, 32.65%.)

(4) *Preparation of tribromolactone from monobromolactone.* To a solution of 5 g. of monobromolactone in 50 c.c. of glacial acetic acid 5 g. of bromine was added in the cold, which was readily absorbed and a crystalline substance deposited on standing. The solution was kept cool over night and the crystalline substance was filtered, washed with cold glacial acetic acid then with ether. Yield 8.3 g. (91% of the theoretical). The tribromolactone, thus prepared, melted at 209° (with decomposition), insoluble in alkali, ether, ethyl alcohol, chloroform and glacial acetic acid and sparingly soluble in boiling alcohol, benzene and petroleum ether. When recrystallized from boiling alcohol the melting point was elevated to 212° (with decomposition). (Found: C, 29.34; H, 3.25; Br, 58.74. Calculated for $C_{10}H_{13}O_2Br_3$: C, 29.65; H, 3.21; Br, 59.23%.)

(5) *The formation of* p-*cuminic acid from shonanic acid dibromide.* When shonanic acid dibromide (10 g.) was subjected to distillation under reduced pressure

the evolution of hydrogen bromide set in at first and there happened no remarkable change until the temperature of the oil bath attained 200°, when suddenly a vigorous evolution of gas took place and on further heating a fraction boiling at 146°/7 mm. distilled over. This fraction on standing deposited a crystalline substance which was spread over a porous plate to remove liquid substance and then it was recrystallized from 40% ethyl alcohol. It melted at 119–120°. Another crop of crystals was obtained from the filtrate by the addition of water, which also melted at 119° after one recrystallization from 40% ethyl alcohol. The substance bears an acidic characteristic and is inert against permanganate and does not give flame colour reaction of Beilstein, showing the absence of bromine. Acid value 341.2 (0.1716 g. required 10.52 c.c. of 0.102N NaOH), calculated for $C_{10}H_{12}O_2$ 341.5. (Found: C, 73.35; H, 7.57. Calculated for $C_{10}H_{12}O_2$: C, 73.17; H, 7.31%. Analysis of the silver salt: Ag, 39.78. Calculated for $C_{10}H_{11}O_2Ag$: Ag, 39.82%.)

Acid chloride. A mixture of 1.4 g. of the acid and 1.5 g. of phosphorus pentachloride was heated on the water-bath for 20 minutes. The product distilled at 107–109°/15 mm. Yield 0.8 c.c.

Amide. The amide was prepared as usual by the interaction of the acid chloride and aqueous ammonia. It melted at 152–153° when recrystallized from 60% ethyl alcohol.

Among the acids of the formula $C_{10}H_{12}O_2$, *p*-cuminic acid melts at 119–120° and its amide at 152–153°. In order to ascertain that the acid under investigation is identical with *p*-cuminic acid the latter was prepared from *p*-cuminol by kali-fusion.

To molten potassium hydroxide (7 g.) in a nickel crucible, 5 g. of *p*-cuminol was added drop by drop with constant agitation. The reaction product was then treated with water and *p*-cuminic acid produced was liberated in the usual way and recrystallized from alcohol. It melted at 119° and on mixing it with the acid under investigation showed no depression of the melting point. Thus it is evident that the acid obtained by the decomposition of shonanic acid dibromide is *p*-cuminic acid.

IV. Oxidation of shonanic acid dibromide with potassium permanganate. To a well-cooled solution of shonanic acid dibromide (10 g.) in 5% sodium carbonate solution (300 c.c.) dilute permanganate solution ($KMnO_4$ 26 g. in 600 c.c. H_2O) was added drop by drop with constant stirring. The reaction mixture was left over night in an atmosphere of carbon dioxide, filtered from manganese dioxide and the alkaline solution thus obtained was evaporated nearly to dryness on the water-bath. The organic acid liberated by acidification with dilute sulphuric acid was extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and then the solvent was distilled away. The remainder crystallized on cooling in prismatic needles which was purified by washing with chloroform and twofold recrystallizations from absolute alcohol. It melted at 239° (with decomposition). The substance is insoluble in cold alcohol, chloroform, benzene and petroleum ether and soluble in alkali from which the original acid can be regenerated by the addition of mineral acid. The presence of bromine atom in the molecule of the acid was recognized by Beilstein's flame colour reaction. (Found: C, 43.37; H, 5.10; Br, 32.12. Calculated

for $C_9H_{13}O_3Br_3$: C, 43.37; H, 5.22; Br, 31.92%. Analysis of the silver salt: Ag, 30.41. Calculated for $C_9H_{12}O_3BrAg$: Ag, 30.33%.)

The acid being monobasic the third atom of oxygen therein may exist either as a carbonyl or as a hydroxyl oxygen, but as the material was scanty, it was not studied any further.

In conclusion, the author wishes to express his sincere thanks to Prof. Kinzô Kafuku for his kind guidance.

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