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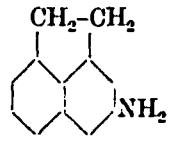
STUDIES IN THE ACENAPHTHENE SERIES. Part III. ω-AMINOACENAPHTHENE AND FURTHER OBSERVATIONS ON *m*-AMINOACENAPHTHENE.

BY GILBERT T. MORGAN AND HERBERT M. STANLEY.

According to the general theory of the constitution of polycyclic aromatic hydrocarbons, acenaphthene should give rise to four amino derivatives, of which the earliest known was the *para*-compound (I.) containing the amino group in position 4 with respect to one of the methylene groups of the aliphatic side chain :—

I.



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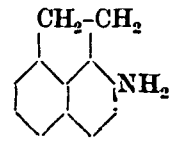

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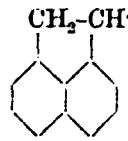
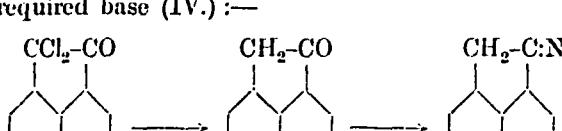


IV.

The *meta*- or 3-aminoacenaphthene (II.) was first described in Part I. of this series of communications (J., 1924, 343 T), the *ortho*- or 2-aminoacenaphthene (III.) formed the subject of Part II. (J., 1925, 408 T), and we have now completed the set of isomerides by preparing *omega*- or 1-aminoacenaphthene, this substance being a base of mixed aliphatic-aromatic type and resembling benzylamine.

Acenaphthenequinone (B.D.C.) was converted into 1:1-dichloroacenaphthenone (V.) which on reduction yielded acenaphthenone (VI.); the oxime (VII.) of this monoketone when reduced gave rise to the required base (IV.) :—

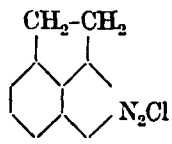


V. VI. VII.

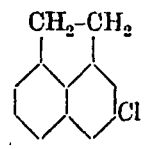
This series of processes constitutes a somewhat laborious method of obtaining ω- or 1-aminoacenaphthene, and attempts were made to synthesise acenaphthenone from naphthalene by condensation with chloroacetyl chloride by the Friedel–Crafts condensation, but the product, although obtained in excellent yield, proved to be *β-naphthyl chloromethyl ketone* (p. 494 T), and accordingly useless for the present purpose.

In the present communication we describe also further experiments on the production and properties of *meta*- or 3-aminoacenaphthene, and the preparation of *para*- or 4-aminoacenaphthene has been effected on a considerable scale.

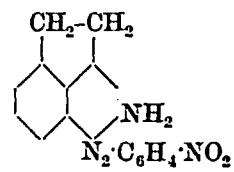
On diazotising its hydrochloride, 3-aminoacenaphthene yields *acenaphthene-3-diazonium chloride* (VIII.), the stability of which when either dry or in solution at ordinary temperatures is greater than that of the naphthalenediazonium chlorides :—



VIII.



IX.



X.

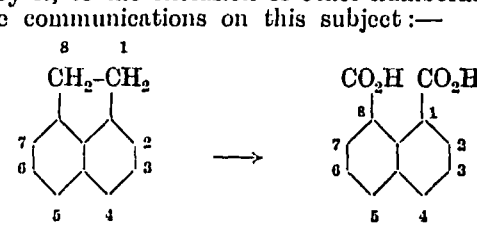
By the Sandmeyer reaction the diazonium salt is converted into *3-chloroacenaphthene* (IX.), a colourless oil.

3-Aminoacenaphthene resembles β-naphthylamine in its reactions with diazonium salts. With *p*-nitrobenzenediazonium chloride the coupling is quantitative and the product has the properties of an aminoazo compound, the constitution of which is indicated provisionally by formula X, although owing to the great reactivity of these aminoacenaphthenes an entry of the diazonium group into position 2 is not excluded. Further experiments on the azo and diazo derivatives of acenaphthene are in progress.

A rational notation for acenaphthene and its derivatives.

Considerable confusion arises in the literature of acenaphthene owing to the circumstance that two systems of notation are in vogue, neither of which is a rational one.

Acenaphthene is structurally a *peri*-di-derivative of naphthalene in which the substituents form an aliphatic side chain, so that as regards constitution the hydrocarbon is *sym*-ethylene-1:8-naphthalene. Hitherto orientation in the acenaphthene series has been demonstrated by oxidising the derivative to the corresponding naphthalic acid (naphthalene-1:8-dicarboxylic acid), and owing to this close connexion between acenaphthene and naphthalene (the latter being the standard of reference), it seems to us to be essential to preserve the same notation in both systems. For this purpose we suggest the following scheme of notation and we propose to employ it, to the exclusion of other numberings, in future communications on this subject :—



Starting with the right hand methylene carbon atom

we number the functional acenaphthene carbon atoms in clockwise order finishing up with the remaining methylene carbon atom. When acenaphthene (or a derivative) is oxidised to naphthalic acid (or a derivative), all the numbers 2 to 7 remain unchanged, but since the methylene carbon atoms have now lost their cyclic positions and have become the substituent carbon atoms of two carboxylic groups their specific numberings are no longer required and become the numberings of the two *peri*- or 1:8-carbon atoms of the naphthalene ring.

Besides maintaining the close connexion between acenaphthene and its prototype, this system of notation has the further advantage of conforming to the terminology adopted in monocyclic systems such as toluene etc. :—

The 2- position indicates the	*ortho*-di-derivative	} CH_3 or CH_2
,, 3- ,, ,,	*meta*-di-derivative	} being in
,, 4- ,, ,,	*para*-di-derivative	} position 1.

The 1-position indicates the ω-derivative, in which the substituent is on the carbon atom of the aliphatic side chain. The advantages of this notation become increasingly obvious in studying the di-derivatives of acenaphthene, where considerable confusion of thought is occasioned by a numbering unconformable with that which is now classical for naphthalene.

EXPERIMENTAL.

I. *ω-Aminoacenaphthene* (IV.).

Acenaphthenequinone (50 g.) was boiled with 59 g. of phosphorus pentachloride (1 mol.) and 200 c.c. of dry toluene for 1¼ hours until a clear solution was obtained. The filtrate on dilution with petroleum (b.p. 40°—60°) yielded 55 g. of dichloroacenaphthenone (83%), which was washed with aqueous sodium bisulphite and crystallised from benzene, when it separated in almost colourless crystals melting at 146° (Graebe and Jequier, Annalen, 1896, **290**, 195).

Ten g. of the dichloro compound in 40 c.c. of warm glacial acetic acid were reduced by the gradual addition of 15 g. of zinc dust. At the end of this reduction the product was completely in solution. Water was added and the mixture distilled in steam, when acenaphthenone (m.p. 121°) passed over, the optimum yield being about 45%.

To a warm solution of 5 g. of acenaphthenone in 40 c.c. of alcohol was added an aqueous solution of 5 g. of hydroxylamine sulphate rendered slightly alkaline by caustic soda. After heating on the water bath for one hour the solution acidified with acetic acid was cooled, when acenaphthenoneoxime separated. Crystallised from benzene the oxime separated in colourless plates melting at 183°—184° (Graebe and Gfeller gave m.p. 175°; Annalen, 1893, **276**, 1). The sodium salt of acenaphthenoneoxime was only sparingly soluble in water.

Reduction of acenaphthenoneoxime.—Reduction of the oxime was difficult; mild agents had little or no effect, more drastic treatment induced hydrolysis. Aluminium-mercury couple in moist ether was ineffective, zinc dust with ammonium chloride in 50% alcohol was somewhat better, but only 10% of basic product was obtained. Titanous chloride or sodium hyposulphite in aquo-alcoholic solutions led to acenaphthenone and ammonia.

Zinc dust and acetic acid gave more of the basic product although admixed with acenaphthene, and this mode of reduction was adopted for the preparation of ω-aminoacenaphthene. Ten g. of zinc dust were added slowly to 6·6 g. of acenaphthenoneoxime in 100 c.c. of 75% acetic acid warmed on the water-bath under reflux. The mixture was then distilled in steam, when about 200 c.c. of distillate yielded a mass of acenaphthene (m.p. 93°—94°) characterised by its picrate (m.p. 162°).

The residual liquid from the steam distillation rendered alkaline, cooled, and extracted with ether yielded an ethereal solution which was dried over sodium sulphate, concentrated to 30 c.c., and saturated with hydrogen chloride, when *ω-aminoacenaphthene hydrochloride* separated as a white deposit (yield 35%). Recrystallised from hot dilute hydrochloric acid the salt was obtained on cooling in colourless plates decomposing partially at 270°. It dissolved readily in hot but was less soluble in cold water. (Found: C, 69·97; H, 6·09; N, 6·95; Cl, 17·35. $C_{12}H_{12}NCl$ requires C, 70·07; H, 5·84; N, 6·81; Cl, 17·28%.)

ω-Aminoacenaphthene picrate, prepared by mixing ethereal solutions of the base and picric acid, separated in well-defined yellow prisms blackening at 240° and melting with evolution of gas at 260°. (Found: C, 54·19; H, 4·18; N, 14·13. $C_{18}H_{14}O_7N_4$ requires C, 54·27; H, 3·52; N, 14·07%.)

ω-Aminoacenaphthene, isolated from its salts with aqueous caustic soda, had a high sublimation pressure for it disappeared rapidly in the desiccator even at the ordinary temperature. A sublimed specimen melted at 135°. It reacted as a strong base, absorbing carbon dioxide in presence of moisture, was very soluble in organic solvents and somewhat soluble in water.

Owing to the difficulty of arriving at ω-aminoacenaphthene from acenaphthenequinone an attempt was made to synthesise acenaphthenone from naphthalene and chloroacetyl chloride, but the experiment was unsuccessful because the Friedel-Crafts condensation led chiefly to β-naphthyl chloromethyl ketone instead of its α-isomeride which might have been induced to condense to acenaphthenone by loss of hydrogen chloride.

β-Naphthyl chloromethyl ketone, $C_{10}H_7{\cdot}CO{\cdot}CH_2Cl$. Anhydrous aluminium chloride (77·5 g.) was slowly added to 50 g. of naphthalene and 47 g. of chloroacetyl chloride in 300 c.c. of carbon disulphide. Hydrogen chloride was evolved and the liquid assumed a deep red colour. After warming for 50 minutes the solvent was distilled off and the viscid residue poured on to ice. The aqueous mixture was subsequently warmed to destroy complex aluminous products, then cooled and extracted with ether. The dried extract was distilled first at the ordinary, then under reduced pressure; the ketone boiled within a few degrees at 185°—187°/10 mm. (yield 55 g. or 69%). The viscid colourless oil slowly congealed to a mass of prismatic needles melting at 30°. (Found: Cl, 17·16. $C_{12}H_9OCl$ requires Cl, 17·34%).

The ketone was insoluble in water but dissolved in the ordinary organic media. Its vapour attacked the mucous membranes of eyes and nose producing a burning sensation with profound irritation.

β-Naphthyl chloromethyl ketone picrate, obtained by mixing alcoholic solutions of its generators, crystallised in pale yellow needles melting at 89°. (Found: picric acid 52·5. $C_{18}H_{12}O_9N_3Cl$ requires 52·8%.)

Various condensing agents were employed on the ketone to induce a condensation with elimination of hydrogen chloride but these were unsuccessful and in no case was any acenaphthenone obtained on steam distillation. These failures raised a suspicion as to orientation of the ketonic side chain. The ketone (10 g.) was oxidised with 20 g. of potassium permanganate and 6 g. of caustic potash. Sulphur dioxide was then passed in until a clear solution was obtained. A white solid which separated on cooling was crystallised from glacial acetic acid, when it proved to be β-naphthoic acid, m.p. 181°. (Found: C, 76·53; H, 4·82; $C_{11}H_8O_2$ requires C, 76·74; H, 4·64%.)

The aqueous filtrate from the oxidation was acidified with hydrochloric acid and concentrated. An oily keto-acid was obtained combining with bisulphite and giving a silver salt, Ag, 34·75%. This product was probably a β-naphthoylformic acid, the silver salt of which should contain 35·15% Ag.

II. *Derivatives of* m-*aminoacenaphthene.*

For the nitration of acenaphthene an enamelled iron pot was employed fitted with glass stirrer, thermometer, and an aperture for adding the nitrating acid. The pot could be cooled or heated at will. Acenaphthene (300 g.) and 2400 c.c. of glacial acid were heated until the hydrocarbon had dissolved. The solution was cooled gradually to 10° and 300 c.c. of nitric acid (*d* 1·42) added slowly with constant agitation and cooling. The nitration was so regulated that, during the first half of the addition of acid, the temperature did not rise above 15°. In the second half of the nitration the temperature was allowed to rise to 30°—35°. The mixture was then cooled and the precipitated nitro compound washed free from acid.

The reduction of *p*-nitroacenaphthene was effected in a cylindrical copper still of 10 litres capacity fitted with screwed-on lid, mechanical stirrer, and adjustable copper condenser. Crude *p*-nitroacenaphthene (200 g.) was dissolved in 2000 c.c. of alcohol and 1000 c.c. of water, and to the hot solution were added 600—700 g. of sodium hyposulphite in lots of 100 g. at a time. The stirring was continuous and the reduction was taken as complete when the foam became colourless. The alcohol was then distilled off for use in subsequent reductions. The residue in the still was poured into a steam-jacketed enamelled evaporating pan containing 15 litres of boiling water, one litre of concentrated hydrochloric acid was added, the mixture boiled for 2 hours and then filtered.

p-Aminoacenaphthene separated from the filtrate after rendering alkaline with ammonia and cooling. Any residue on the filter was again boiled with more hydrochloric acid until all the amine had been extracted. The crude amine was recrystallised from petroleum, b.p. 80°—100°, and then had only a faint yellow colour. From 800 g. of acenaphthene 430 g. of base were obtained, being an over-all yield of 49%.

Formylation of *p*-aminoacenaphthene gave a 96% yield on the foregoing scale but nitration of the formyl derivative was practicable only on a smaller scale, 25 g. of this compound being dissolved in 100 c.c. of warm glacial acetic acid and the solution cooled to 10°; 15 c.c. of nitric acid (*d* 1·4) were slowly added, followed by 15 c.c of the same acid added at once. The temperature rose to 45°; 22 g. of nitroformyl-*p*-aminoacenaphthene were obtained, or 77% of theory. Hydrolysis of the nitro compound was accomplished by boiling alcoholic hydrochloric acid. The replacement of amino group by iodine through the diazo group was carried out as in our former communication (J., 1924, 43, 343 T), the yield of crude 3-nitro-4-iodoacenaphthene being 55%.

The final stage of reduction was carried out as before (*loc. cit.*) and *m*-aminoacenaphthene isolated as its picrate, yield 60%.

Acenaphthene-3-diazonium chloride (VIII.).

To a solution of 1·25 g. of *m*-aminoacenaphthene in 40 c.c. of glacial acetic acid were added 2 c.c. of concentrated hydrochloric acid, forming a suspension of white *m*-aminoacenaphthene hydrochloride. This mixture cooled to 0° was treated with 0·6 g. of sodium nitrite in 7 c.c. of water, when a clear yellowish-red diazo solution was obtained. After a few minutes a yellow crystalline precipitate of diazonium chloride separated which was washed successively with water and alcohol and dried over sulphuric acid. (Found: Cl, 15·15, 15·33; N, 11·6. $C_{12}H_9N_2Cl,H_2O$ requires Cl, 15·12; N, 11·95%.) This yellow diazonium salt was kept for 24 hours without change, but subsequently it began to lose nitrogen; it decomposed quietly at 150°—160°. When warmed to 120° for one hour it lost nearly 90% of its water of crystallisation, but in another hour a portion of the nitrogen was also evolved.

m-*Chloroacenaphthene* (3-*chloroacenaphthene*) (IX.).

Three g. of *m*- or 3-aminoacenaphthene were diazotised as above in hydrochloric and acetic acids and the solution added slowly to a cuprous chloride solution at 50° prepared by dissolving 5 g. of copper carbonate in 50 c.c. of strong hydrochloric acid and boiling with copper turnings until the liquid was nearly colourless. The mixture was heated on the water bath until evolution of nitrogen ceased and then distilled in steam. The oily distillate was extracted with ether. The dried ethereal distillate after removing solvent yielded 1·2 g. of a colourless oil of pleasant odour and not boiling below 290° but blackening at 250°; it could not be caused to crystallise even in a freezing mixture. Owing to its oily nature 3-chloroacenaphthene was converted into its picrate by mixing alcoholic solutions of the two generators.

3-*Chloroacenaphthene picrate* separated from alcohol in orange crystals melting at 79°—80°; it was resolved into its components by boiling in light petroleum. (Found: Cl, 8·55; picric acid, 54·6. $C_{18}H_{12}O_7N_3Cl$ requires Cl, 8·49; picric acid, 54·9%.)

4′-Nitrobenzeneazo-3-aminoacenaphthene (X.).

A diazo solution from 0·4 g. of *p*-nitroaniline freed from excess of nitrous acid by urea was added slowly with stirring to a solution of 0·5 g. of 3-aminoacenaphthene in 30 c.c of glacial acetic acid containing 5 g. of sodium acetate dissolved in 10 c.c of water. The bronzy-red precipitate (88%) was washed with ammonia and water and crystallised from glacial acetic acid, when it separated in bronzy-red crystals with a green reflex. (Found: N, 17·30. $C_{18}H_{14}O_2N_2$ requires N, 17·61%.) With concentrated sulphuric acid this aminoazo derivative developed a deep blue coloration but gave no colour change with alcoholic soda; it melted at 200°.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has helped to defray the expense of this investigation; and to Messrs. Hardman and Holden, of Miles Platting, Manchester, for a gift of acenaphthene.

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Edgbaston.

LÆVO-CAMPHOR-10-SULPHONIC ACID FROM SYNTHETIC CAMPHOR.

BY HENRY BURGESS AND CHARLES STANLEY GIBSON.

Pope and his co-workers (Chem. Soc. Trans., 1910, **97**, 2199 and subsequent papers) showed that the resolution of many externally compensated bases is much more easily accomplished when both the *d*- and *l*-forms of the various sulphonic acids derived from camphor are used than when only the ordinary, or *d*, form is available. For some considerable time it has been impossible to obtain the naturally occurring *l*-camphor, but synthetic camphor (produced by various processes from pinene) is a commercial article. Synthetic camphor is almost optically inactive, and it has become necessary to study the possibility of obtaining from it the *l*-forms of the various sulphonic acids of camphor which are so greatly needed in connexion with stereochemical investigations.

Pope and Read (Chem. Soc. Trans., 1910, **97**, 992) have already described the successful resolution of externally compensated camphor-π-sulphonic acid by means of strychnine. In the first place we have investigated the production of *l*-camphor-10-sulphonic acid (Reychler, Bull. Soc. chim., 1898, [iii], **19**, 120; Armstrong and Lowry, Chem. Soc. Trans., 1902, **81**, 1469; Wedekind, Schenk, and Stüsser, Ber., 1923, **56**, 633; Lipp and Lausberg, Annalen, 1924, **436**, 274; Burgess and Lowry, J. Chem. Soc., 1925, **127**, 279) from synthetic camphor by a method which can be used on a moderately large scale.

Rewald (Ber., 1909, **42**, 3136) resolved externally compensated camphor-10-sulphonic acid into its optically active components by neutralising the inactive acid with brucine and separating the two salts, brucine-*d*-acid and brucine-*l*-acid, the former being the less soluble. The two salts not only required six crystallisations from water for complete purification but, in order to obtain the *l*-acid, it had still to be isolated from its brucine salt and subsequently recrystallised twice from acetic acid. Even then the *l*-acid obtained still contained an appreciable quantity of the *d*-acid, and altogether it appeared that this method was unsuitable for producing large quantities of the pure *l*-acid.

Before proceeding to the actual resolution of the inactive acid it was necessary to determine the solubilities of the salts of the optically active acids with such alkaloids as would ordinarily be easily available. Brucine and strychnine were found to be the most suitable, the solubilities of the salts in g. per 100 g. of water at 8·5° being as follows: brucine-*d*-acid, 1·783; brucine-*l*-acid, 5·904; strychnine-*d*-acid, 3·205; strychnine-*l*-acid, 3·053. These figures indicated that the method adopted for the resolution of acyl derivatives of α-amino-acids (Pope and Gibson, Chem. Soc. Trans., 1912, **101**, 939; Gibson and Simonsen, *ibid.*, 1915, **107**, 798; Colles and Gibson, J. Chem. Soc., 1924, **125**, 2505) might be employed in this case also. When the inactive acid was neutralised with half an equivalent of brucine and half an equivalent of ammonia the brucine-*d*-acid salt separated to the extent of 87% of the theoretical quantity and was optically pure after two crystallisations from water. The acid obtained from the mother liquor after separating the brucine-*d*-acid was then treated with sufficient strychnine to neutralise the calculated amount of *l*-acid present and ammonia to neutralise the *d*-acid. The strychnine salt which separated had a constant rotatory power after one crystallisation from water, and this was appreciably lower than that of the pure strychnine-*l*-acid prepared for the solubility determinations. It obviously consisted of mixed crystals of the two salts, strychnine-*l*-acid and strychnine-*d*-acid, which cannot be separated by crystallisation from water. This was confirmed in other experiments, and showed the impossibility of using strychnine for the resolution.

During the work it was found that the acid obtained in the usual manner from the above strychnine salt and which contained an excess of the *l*-acid, on recrystallisation from ethyl acetate, became free from the *d*-isomeride. The method which has been applied with success for obtaining the *l*-acid in quantity consequently consists in removing most of the *d*-acid by means of brucine, as described above, and then subsequently crystallising the acid obtained from the mother liquor until its rotatory power is constant. Five crystallisations from ethyl acetate have been found to be sufficient working on the laboratory scale.

Experimental.

For the determination of their solubilities the following salts were prepared by neutralising the pure acid with the calculated quantity of the requisite

alkaloid in aqueous solution and recrystallising the salt from water. The salts were dried in the air and the solubilities were determined in the usual manner at 8·5°, the temperature in the ice-chest.

Brucine d-*camphor*-10-*sulphonate*.—0·2363 g. was contained in 13·4913 g. of solution. Solubility= 1·783 g. per 100 g. of water.

Brucine l-*camphor*-10-*sulphonate*.—0·6081 g. was contained in 12·5470 g. of solution. Solubility= 5·094 g. per 100 g. of water. M.p., 251°—253° (with previous charring). $[\alpha]_{5461}$ 35·0°* (c=1·767). (Found C=63·5, H=7·0: $C_{33}H_{42}O_8N_2S$ requires C= 63·2, H=6·8%.

Strychnine d-*camphor*-10-*sulphonate*. — 0·3663 g. was contained in 11·7940 g. of solution. Solubility= 3·205 g. per 100 g. of water. M.p., 275°–278° (with previous charring). $[\alpha]_{5461}$ −13·7° (c=1·242, anhydrous). Found: air-dried material H_2O=3·1, anhydrous material C=65·7, H=6·7: $C_{31}H_{38}O_6N_2S,H_2O$ requires H_2O=3·1%; $C_{31}H_{38}O_6N_2S$ requires C=65·7, H=6·8%.

Strychnine l-*camphor*-10-*sulphonate*. — 0·3556 g. was contained in 12·0019 g. of solution. Solubility= 3·053 g. per 100 g. of water. $[\alpha]_{5461}$ −37·9° (c=2·070, anhydrous).

The synthetic camphor was converted into the camphor-10-sulphonic acid under the conditions described by Reychler (*loc. cit.*), 960 g. in three lots being a convenient quantity to work with in the laboratory. The yield of the anhydrous acid after recrystallisation from ethyl acetate is only 34% of the theoretical quantity, and we are still investigating this point. The acid used in the investigation was free from sulphuric acid and had $[\alpha]_{5461}$ +0·205° (c= 34·0); it may therefore be considered optically inactive for all practical purposes.

Only typical experiments illustrative of the method of resolution will be described.

Separation of d-*camphor*-10-*sulphonic acid from the inactive material.*

The inactive acid (467 g.) was dissolved in 700 c.c. of water, and to this were added 280 c.c. of 3·625 *N* ammonia solution (½ mol.) and then 467 g. of brucine (½ mol.) so that complete solution of the whole was effected in about 1·5 litres of water at the boiling point. The solution was allowed to cool slowly until crystals began to separate, when it was stirred thoroughly for some time and then allowed to stand for 18 hours in the ice-chest. The brucine salt was filtered off (the filtrate *A* was worked up later), washed with a little water, and after two crystallisations from water found to be pure, $[\alpha]_{5461}$ −15·9°, yield 505 g. In this particular case it was mixed with another similar specimen, and the total quantity (670 g., having $[\alpha]_{5461}$ −15·7°) was further recrystallised from water (960 c.c.) for the final determination of the constants.

Brucine d-*camphor*-10-*sulphonate* crystallises from water with two molecules of water of crystallisation which are not lost until the material is heated for some time at 140°. Found: air-dried material H_2O=5·2, anhydrous material C=63·0, H=6·8; $C_{33}H_{42}O_8N_2S,2H_2O$ requires H_2O=5·4%; $C_{33}H_{42}O_8N_2S$ requires C=63·25, H=6·75%. The air-dried material has $[\alpha]_{5461}$ −15·1° and $[\alpha]_{5780}$ −12·9° (c=1·610). If heated slowly it melts with previous charring at 276°–278°, but it melts with evolution of gas (loss of water ?) if plunged into a bath at 160°.

To obtain the pure *d*-acid, 638 g. of the air-dried pure brucine salt were dissolved in 800 c.c. of boiling water and a slight excess of aqueous ammonia was added. The brucine, which crystallised out on cooling, was filtered off and thoroughly washed with water. The filtrate and washings were extracted with chloroform until free from brucine and then boiled with an excess of baryta (240 g.) until ammonia was no longer evolved and the solution remained slightly alkaline. To the boiling filtrate was added a slight excess above the calculated quantity of sulphuric acid to precipitate all the barium as sulphate. The barium sulphate was filtered off and the filtrate decolorised with animal charcoal, and then evaporated almost to dryness on the water bath. On recrystallisation from a total quantity of 650 c.c. of purified ethyl acetate three fractions of the acid were obtained having $[\alpha]_{5461}$ +27·6°, +27·9°, and +28·3°, respectively, the total weight being 210 g. On mixing these three fractions and recrystallising from ethyl acetate there was no appreciable change in rotatory power. The amount obtained in this particular experiment represents 94% of the acid present in the brucine salt and 66% of the *d*-acid in the inactive acid originally taken.

The pure *d*-acid obtained had $[\alpha]_{5461}$ +28·27° and $[\alpha]_{5780}$ +22·63°, whereas the *d*-acid prepared directly from *d*-camphor showed in two determinations $[\alpha]_{5461}$ +28·06° and +28·17°, $[\alpha]_{5780}$ +22·40° and +22·15° (c=5·30 and 5·36 respectively). Pope and Gibson (Chem. Soc. Trans., 1910, 97, 2214) found $[\alpha]_D$+21·63° for the same acid.

Separation of l-*camphor*-10-*sulphonic acid.*

The acid was obtained from filtrate *A* (see above) in the same manner as for the isolation of the *d*-acid, care being taken in this case to avoid excess of sulphuric acid. The colourless solution of the acid was evaporated to known bulk, a portion titrated with standard sodium hydroxide, and its rotatory power determined. The solution contained 195·1 g. of the sulphonic acid per litre and had $[\alpha]_{5461}$ −21·08°. Assuming $[\alpha]_{5461}$ −28·15° for the pure *l*-acid, the amount of *l*-acid is calculated as 87·5% of the total sulphonic acid present in the solution.

Of this solution 994 c.c. were treated with 252 g. of strychnine (by an oversight this is approximately 3% more than the theoretical amount, equivalent to the *l*-acid present) and 22·5 c.c. of aqueous ammonia (strength as before, 3% deficiency for the *d*-acid present) and the whole brought into solution at the boiling temperature with the addition of another 100 c.c. of water. The crystals which separated had after recrystallisation from 500 c.c. of water $[\alpha]_{5461}$ −32·8° (c=2·634) and, when recrystallised again from water, the rotatory power was practically

*All rotatory powers were determined in aqueous solution at 18°-20° using 4-dm. tubes. Except where air-dried material is specially mentioned only guaranteed anhydrous material was weighed out in all cases.

unchanged ($[\alpha]_{5461}$ −32·96°). The salt melts at 273° with previous charring and, if plunged into a bath at 190°, it melts with evolution of gas and resolidifies on cooling. This phenomenon does not occur at 188°. (Found: air-dried material, H_2O=3·3; anhydrous material, C=65·4, H=6·65; $C_{31}H_{38}O_6N_2S$, H_2O requires H_2O=3·1%, $C_{31}H_{38}O_6N_2S$ requires C=65·7, H = 6·8%.) Since the rotatory power was constant and lower than that of the pure strychnine-*l*-acid (see above) it was clear that the material consisted of mixed crystals of the two salts, strychnine-*l*-acid and strychnine-*d*-acid, which cannot be separated by fractional crystallisation from water. Further, the acid obtained from the strychnine salt in the usual manner had a lower rotatory power than that of the pure *l*-acid, and the impossibility of separating the two salts by fractional crystallisation from water was further proved by the following experiments.

Sixty g. of the strychnine salt obtained from an experiment such as that just described had the following rotatory powers after each of five successive crystallisations from water: $[\alpha]_{5461}$ −32·7°, −33·5°, −33·4°, −33·8°, −33·9°. The rotatory power remained constant and, by calculation, the last fraction contained 84% of the pure strychnine-*l*-acid salt. The acid obtained from this salt would not be any more pure than that before treatment with strychnine.

A specimen of the strychnine salt (106 g.) having $[\alpha]_{5461}$ −27·0° was recrystallised from water and mixed with 171 g. having originally $[\alpha]_{5461}$ −29·4°, also once recrystallised from water. The resulting 241 g. were recrystallised eight times from water. After four crystallisations, it had $[\alpha]_{5461}$ −29·3°, after six crystallisations, −29·4°, after eight crystallisations, −29·5°, the weight of the final fraction being only 58 g.

It was hoped that the crystallisation from water of a suitable metallic salt would aid the purification of the crude *l*-acid. Of those which might prove suitable for such a purpose, 3·5 g. of the barium salt of the *l*-acid remained dissolved in 10 c.c. of its aqueous solution, 11 g. of the lead salt remained dissolved in 14 c.c. of its aqueous solution, whilst the mercury salt was too sparingly soluble and appeared to hydrolyse with deposition of mercury except in acid solution.

Having found that recrystallisation of the crude *l*-acid from ethyl acetate quickly raised its rotatory power, it was soon evident that complete purification could be effected by this means. The method of complete resolution which has now been adopted may be described by one typical experiment.

A solution of the inactive acid (245 g.) in water (350 c.c.) having been carefully neutralised with ammonia was mixed with a solution of 245 g. of the inactive acid in 350 c.c. of water, and to this were added in small portions 493 g. of brucine (recovered from previous experiments). The total volume of the boiling solution was 1600–1700 c.c. As soon as crystals began to form on cooling, the solution was well stirred until it was almost pasty and then left to stand in the ice-chest for about 18 hours. The brucine salt was filtered off, washed several times with a little water (total volume of filtrate, B_1=1425 c.c.), and the brucine salt recrystallised from the minimum volume of boiling water. The air-dried material had $[\alpha]_{5461}$ −14·9° and weighed 522 g. The filtrate B was combined with the mother liquor from the recrystallisation of the brucine salt and the acid liberated from this solution in the manner previously described, a slight excess of sulphuric acid being purposely used in decomposing the barium salt. The solution of the sulphonic acid was evaporated carefully to dryness and the resulting product crystallised from ethyl acetate. After five crystallisations its rotatory power was constant, $[\alpha]_{5461}$ −28·3° and −28·5° (c=5·032 and 4·772 respectively), and equal and opposite to that of pure *d*-camphor-10-sulphonic acid. 126·5 g. of pure *l*-acid were obtained corresponding to 51·5% of the *l*-acid present in the inactive acid used. The acid obtained from the mother liquors (about 140 g.) was not purified sufficiently quickly by crystallisation from ethyl acetate and, in working up large quantities, it is first treated with brucine so as to remove the major quantity of the *d*-acid present.

The investigation of convenient methods for producing the other *l*-sulphonic acids derived from camphor is being continued.

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