

CXXIII.—*The Constituents of the Sandarac Resins.*

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THE sandarac of commerce is derived from the plant *Callitris quadrivalvis* which occurs in the plant family *Cupressineæ*, a subdivision of the *Coniferae*. Like most plants of this order, the various species of *Callitris* secrete an oleo-resin, which at certain seasons of the year exudes from the stem, and by evaporation of a portion of its contained volatile matter forms small, hard masses of resin technically known as "tears." It is in this form that sandarac occurs in commerce, the "tears" being long and narrow, having a glassy fracture, and a pungent, aromatic, and slightly bitter taste. The resin is employed in the manufacture of some of the finer kinds of spirit varnishes, and in the form of a powder for dusting on the surface of parchment to increase its absorptive power for ink.

There also appears on the market from time to time a similar resin, which, since it is exported from Australia, is commonly known as "white pine resin," or "Australian sandarac." This substance is the natural exudation product of *Callitris verrucosa*, and differs from the common sandarac chiefly in the larger size of its "tears" and its smaller solubility in alcohol.

It was with the object of comparing the constituents of these two resins that the present investigation was undertaken.

The chemical constituents of the resins of the various species of *Pinus* have been the subject of many investigations, but the less known members of the *Coniferae* have been somewhat neglected in this respect, so that the literature of the present subject is meagre.

The first important paper dealing with the chemistry of sandarac is that of Johnston (*Phil. Trans.*, 1839, 129, 239), who asserts that the resin contains three acids differing in their solubilities in alcohol and in those of their potassium salts in alcoholic potash. These acids were isolated in the following way. The resin was exhausted with alcohol, leaving an insoluble, yellow, amorphous powder, soluble in ether and having a composition represented by the formula $C_{40}H_{31}O_5$. This the author calls A resin. The alcoholic extract was then treated with solid potash, whereby an insoluble potassium salt was obtained. This, on solution in water and addition of hydrochloric acid, gave B resin, which is similar in appearance to the A resin, but is soluble in alcohol, and has a composition represented by the formula $C_{40}H_{31}O_6$. The portion soluble in alcoholic potash gave, on regeneration with acids, a mixture of two resins, of which one, soluble in alcohol and on combustion giving numbers corresponding with those required for the formula $C_{40}H_{30}O_6$, is named C resin; whilst the other, insoluble in alcohol, is regarded as identical with A. No attempts were made by the author to crystallise these substances, nor were any well-defined derivatives obtained from them.

The only other paper of interest is that of Tschirch and Balzer (*Arch. Pharm.*, 1896, 234, 291). These authors adopted a slight modification of Johnston's method for the separation of the constituents, namely, they dissolved the resin in aqueous potash, and to this solution added solid potash, so precipitating an insoluble potassium salt, from which was regenerated, by solution in water and addition of hydrochloric acid, an amorphous resin which was named *sandaracolic acid*. This substance is said to be obtained in a crystalline condition by allowing its alcoholic solution to stand for a long time. The crystals melted at 140° , and on combustion numbers were obtained agreeing with those required by the formula $C_{45}H_{66}O_7$. The molecular weight was determined by Raoult's freezing point method, and the curious results obtained by the authors are tabulated below. In calculating M from

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the experimental data, evidently some arithmetical error has been made by the authors, as is shown by the recalculated values of M given in the tabular statement ($C_{45}H_{66}O_7$ requires $M = 718$).

Weight of solvent used (phenol).	Weight of substance used.	Depression of freezing point.	Molecular weight calculated by Tschirch and Balzer.	Molecular weight recalculated.
28·85	0·255	1·00°	660	65
25·102	0·200	0·49	645	120
25·10	0·260	0·12	690	638

Such arithmetical errors frequently occur throughout the paper, and will be pointed out as they arise. By titration experiments with normal potash, the authors find that this acid is monobasic, yet they assign without comment to the copper salt, obtained by double decomposition between copper sulphate and the sodium salt, a formula representing it as that of a dibasic acid, namely, $C_{45}H_{64}O_7Cu$. The silver salt was also prepared by the addition of excess of ammonia to sandaracolic acid and the further addition of ammoniacal silver nitrate solution. On standing for some weeks, this solution deposited a precipitate which was found to contain 12·84 per cent. of silver; $C_{45}H_{65}O_7Ag$ requires 13 per cent. By the action of acetic and benzoic anhydrides, monoacetyl and monobenzoyl derivatives respectively were obtained, but only in an amorphous condition. By the action of hydriodic acid in Zeisel's apparatus, evidence of the existence of a methoxyl group in the acid was obtained, whilst oxidation with nitric acid gave picric and oxalic acids. Fusion with potash gave a substance resembling resorcinol. From the potassium salt soluble in excess of potash, was isolated by the addition of hydrochloric acid, a second resin, to which the name callitrolic acid was given. This acid was with difficulty obtained in a crystalline condition by conversion into its amorphous lead salt and regeneration by sulphuretted hydrogen. The crystallised acid melted at 248° , and, on combustion, the following results were obtained:

(i) $C = 77·79$, $H = 8·63$; (ii) $C = 77·58$, $H = 8·30$.

$C_{65}H_{84}O_8$ requires, according to the authors' calculations, $C = 77·3$, $H = 8·43$ per cent.

In reality, this formula requires $C = 78·6$, $H = 8·4$ per cent., and the results obtained by the authors are better represented by the formula $C_{62}H_{80}O_8$, where $C = 78·15$, $H = 8·40$ per cent.

The molecular weight was determined by the freezing point method, and found to agree with that required by the formula $C_{65}H_{84}O_8$. The

same carelessness in calculation is shown here, thus: 22.14 grams of phenol, containing 0.331 gram of the acid, gave a depression 0.12° . According to the authors, this corresponds to a molecular weight 952; in reality, the calculated value is 921, but this is sufficiently near that required by the formula $C_{65}H_{84}O_8$ to be within experimental error. Callitrolic acid was also found to be monobasic, yet the authors assign to its copper salt the formula $C_{65}H_{82}O_8Cu$, which is that of a salt of a dibasic acid. On subjecting the crude resin to steam distillation, a quantity of a brown oil having an odour of pine trees was obtained, but was not further examined. Since the appearance of the above paper, Tschirch, in a note appended to a paper on another subject, mentions that he has isolated from sandarac a new crystalline acid by shaking an ethereal solution of the resin with sodium carbonate (Dieterich, *Analyse der Harz, Berlin*, 1900), but no further information regarding this acid has been published.

It will be convenient to include in this account of previous work on this subject a short *résumé* of the work so far accomplished on pine resins, since, as will be seen later, the constituents of sandarac bring it into close relation with this class.

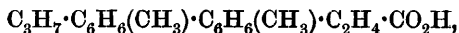
From commercial colophony there have been isolated by various workers, *sylvic*, *sylvinic*, *isosylvinic*, *pimaric*, *pinic*, and *abietic* acids, but the researches of Liebermann (*Ber.*, 1884, 17, 1884), Haller (*Ber.*, 1885, 18, 2165), Maly (*Annalen*, 1869, 149, 115, 161, 244), and especially of Mach (*Monatsh.*, 1893, 14, 186; 1894, 15, 627), show clearly that most of these substances are merely impure forms of abietic acid. Mach examined a large number of specimens of American and French colophony and of "galipot," and in each case he was only able to isolate *abietic acid*, $C_{19}H_{28}O_2$. On the other hand, Vesterberg, in his researches on the constituents of "colophonium de Bordeaux" (*Ber.*, 1885, 18, 3331; 1886, 19, 2167; 1887, 20, 3251), found that this resin contained two isomeric crystalline acids of the formula $C_{20}H_{30}O_2$, to which he gave the names *d*- and *l*-*pimaric acids*. Whilst Mach could not obtain these substances from the Bordeaux colophony now obtainable in commerce, he was able, by an examination of a specimen of *d*-pimaric acid supplied to him by Vesterberg, to confirm the results of the latter.

These results are perhaps to be explained on the assumption that American colophony has, in European commerce, almost replaced the French product, whilst the American "thus" is now commonly sold in place of "galipot."

In a more recent investigation of Bordeaux turpentine by Tschirch and Bruenig (*Chem. Centr.*, 1900, ii, 1270), it was found that this resin contains two crystalline acids, pimaric acid (m. p. $114-118^{\circ}$) and pimaric acid. The latter, isolated by treating the resin with soda

solution, was optically inactive, whilst the pimaric acid, isolated from a specimen of Bordeaux colophony by crystallisation from alcohol, was strongly lævorotatory. The optical inactivity of the first-mentioned specimen of acid is accounted for by the authors on the assumption that racemisation occurs with the conversion into the sodium salt. These results are in direct opposition to those of previous workers—thus, Vesterberg used the sodium salts of *d*- and *l*-pimaric acids as a means of isolating and purifying these substances, and the products so obtained were optically active. Further, it should be pointed out that, although the authors give a certain amount of evidence for the statement that pimaric acid is a new substance, they content themselves as regards pimaric acid with the assertion that they obtained it, and give no details as to how they identified it. Since no account of an inactive pimaric acid has, so far, appeared in chemical literature, it is curious that no attempt was made to characterise this substance when opportunity offered.

Attention should also be drawn to the work of Bruylants on the destructive distillation of colophony (*Ber.*, 1875, 8, 1463; 1878, 11, 447). This author obtained in this way ethylene, propylene, and amylene, and by the destructive distillation of calcium pimarate, similar compounds, together with methyl ethyl ketone, diethyl ketone, toluene, dimethylbenzene, terebene, and diterebene. He infers from these observations that the constitution of pimaric acid may be represented by the formula



which is that of a carboxyl derivative of a diterpene.

In a similar manner, Bischoff and Nastvogel (*Ber.*, 1890, 23, 1921) obtained, by destructively distilling colophony in a vacuum, an oily hydrocarbon boiling at 216—225°, and a volatile resin to which they give the name *isosylvinic anhydride*, since, on treatment with sodium hydroxide, it gave the sodium salt of an acid isomeric with sylvinic acid, $\text{C}_{20}\text{H}_{30}\text{O}_2$. To the oily hydrocarbon which they regarded as identical with the colophene of Deville (*Ann. Chim. Phys.*, 1840, [ii], 75, 37) and Riban (*Ann. Chim. Phys.*, 1875, [v], 6, 40), they ascribe a constitution, which is that of a condensed dihydrocymene, whilst they further represent *isosylvinic acid* as a carboxy-derivative of colophene, and the anhydride as formed by the condensation of two molecules of the acid.

It will be seen that such a formula closely resembles that suggested by Bruylants. Similar evidence of the aromatic character of the nucleus of the acid of colophony is given by Ciamician, who obtained, by distillation of this resin with zinc dust (*Ber.*, 1878, 11, 269), such substances as toluene, naphthalene, methylnaphthalene, and methyl-

anthracene. Further, Wallach and Rheindorff (*Annalen*, 1892, 271, 285) find that colophony, on destructive distillation, yields pinene and dipentene.

EXPERIMENTAL.

Extraction of the Volatile Oil.

The crude resin was dissolved in alcohol, and the solution made alkaline by the addition of alcoholic potash in slight excess. The alcohol was then removed by distillation, the residual semi-solid mixture of potassium salts dissolved in water, and the solution shaken out with ether. Preliminary experiments having shown that the volatile oil of the plant consisted only of hydrocarbons, the ethereal solution so obtained was next dried over solid potash, which removed, besides water, a small amount of resinous matter. The ether was then removed by distillation, and the residue fractionally distilled. In general, it was separated into three portions, having the following range of boiling points: 150—180°, 180—220°, and 220—280°. From the first of these, a large fraction boiling from 150—160° could be obtained, which on redistillation over metallic sodium gave a portion boiling from 152—159°. The fraction 180—220° evidently was a mixture, but it was found impossible to get even a partial separation of its constituents, since on distillation the temperature rose fairly rapidly and regularly between the two limits mentioned. The fraction 220—280°, on rectification over metallic sodium, came over mostly from 260—280° as a slightly viscous, colourless oil, having an odour faintly recalling that of peppermint. With the small quantities of volatile oil obtainable, it was impracticable to attempt by further fractionation to obtain purer products than these two fractions. Their examination was therefore proceeded with.

Fraction boiling between 152° and 159°.

This fraction was a colourless liquid with a pleasant, pine-like odour. Its density at 15°/15° was 0.8588 [pinene 0.8586].

Determinations of the optical activity of the fraction in a 100 mm. tube with a Laurent's polarimeter, using sodium light, gave +18°27' as the mean of ten observations, whence $[\alpha]_D + 21^\circ 30'$.

Action of Nitrosyl Chloride.—To a few c.c. of the fraction the same quantity of amyl nitrite was added, and sufficient glacial acetic acid to form a clear solution, which was then cooled by immersion in a mixture of sodium sulphate and hydrochloric acid. To the solution was added, drop by drop, strong hydrochloric acid so long as a blue colour was produced, which disappeared on cooling and shaking. After a few minutes, a crop of crystals separated. These were removed by

filtration, and recrystallised by addition of methyl alcohol to their chloroform solution. The substance so obtained formed silky masses of minute needles melting at 103° when heated slowly. For purposes of comparison, a specimen of pinene nitrosyl chloride was prepared from commercial turpentine by the method described above. This presented a similar appearance to that obtained from sandarac oil, and melted at the same temperature under the same conditions.

Preparation of the Nitropiperidide.—The nitrosyl chloride of the hydrocarbon was dissolved in a little alcohol, and a slight excess of piperidine was added to the solution, which was then warmed on the water-bath for a few minutes. To the mixture, water was added, causing the precipitation of a heavy, oily liquid. The excess of water was poured off, and the oil dissolved in alcohol and set aside. After several days, a small quantity of a substance crystallising in needles and melting at 118° , after recrystallisation from alcohol, was obtained. A specimen of pinene nitrol piperidide, obtained in like manner from pinene nitrosylchloride, melted at 118° .

The fraction of lower boiling point from sandarac oil is therefore composed chiefly of *d*-pinene.

Fraction boiling between 260° and 280° .

This portion of the volatile oil, when freshly distilled over metallic sodium, is a colourless, somewhat viscous liquid, but on standing it slowly assumes a greenish colour and shows slight signs of resinification. Its density at $15^{\circ}/15^{\circ}$ was 0.9386.

From its boiling point and general behaviour it was apparently a sesquiterpene or a diterpene, and further examination showed the latter supposition was most probably correct.

The oil is dextrorotatory. A determination of the specific rotation in a 100 mm. tube, using sodium light, gave $+51^{\circ}42'$ as the mean of ten observations, whence $[\alpha]_D +55^{\circ}$.

The refractive index was determined by means of an Abbé refractometer and gave $\mu = 1.5215$ as the mean of ten observations.

On analysis, the following result was obtained :

0.1237 gave 0.400 CO_2 and 0.128 H_2O . C = 88.1 ; H = 11.4.

$\text{C}_{20}\text{H}_{32}$ requires C = 88.3 ; H = 11.7 per cent.

A determination of the vapour density by Victor Meyer's method, using anthracene vapour as the heating agent, gave the molecular weight = 262 ; $\text{C}_{20}\text{H}_{32}$ requires 272.

Ethereal solutions of this hydrocarbon do not absorb hydrogen chloride, but they decolorise bromine with evolution of hydrogen bromide.

A satisfactory bromine derivative has not been obtained, the product being an oil which does not crystallise from solvents or become crystalline when kept at low temperatures. On heating, even in a vacuum, it decomposes, giving resinous products, so that no method has been found of obtaining it in a pure state.

The hydrocarbon does not combine with either nitrosyl chloride or nitrogen trioxide. In several attempts to prepare such derivatives by the usual methods no combination occurred, and the unaltered substance was recovered at the end of the experiments. On adding strong sulphuric acid, drop by drop, to a solution of the hydrocarbon in glacial acetic acid, a deep violet colour is produced, which disappears on warming.

The physical constants of this oil show that it does not belong to the class of sesquiterpenes, but probably to the diterpenes. The properties of the latter class of substances are so far but imperfectly known. The constants given in the following table are those ascribed to the few diterpenes which have been isolated. For convenience of comparison, the constants usually characteristic of the sesquiterpenes are also added :

	Relative density.	Vapour density.	Refractive index.	B. p.	Action of HCl.
Sesquiterpenes.....	0.9001—0.918	7.23	1.501	240—260°	Forms additive products.
Diterpenes.....	0.938	9.6	—	260—315	No action.
Sandarac hydrocarbon.....	0.9386	9.28	1.5215	270—280	No action.

It will be seen on comparing the constants of these various substances as given in the table that the characters of the hydrocarbon of high boiling point of sandarac oil are in general agreement with those of the diterpenes, and that it must be regarded as a member of this class of compounds.

Inactive Pimaric Acid.

The mixture of potassium salts of the resin acids, after treatment with ether for the removal of the volatile oil, was warmed to remove the dissolved ether, and to the aqueous solution a 20 per cent. solution of potash was added until no further precipitation occurred. The slimy precipitate rapidly settled to a semi-solid mass, from which the supernatant liquid could be readily poured off. The precipitated potassium salt was then dissolved in water, strong hydrochloric acid added in excess, and the semi-solid mixture poured upon a calico filter, washed free from acid, and dried in a current of warm air. When

quite free from moisture, it was treated with 90 per cent. alcohol, when it was found that a considerable portion of the resin was no longer soluble in that medium. The insoluble matter was filtered off, the filtrate made alkaline with alcoholic potash, and the solvent removed by distillation. With the residue, the precipitation of the potassium salt and the regeneration of the resin, as already described, was repeated until a resin quite soluble in alcohol was obtained. If to this alcoholic solution of the purified resin sufficient water be added to produce a slight turbidity, and the mixture be set aside for several days, a crop of crystals is obtained which when recrystallised melt at 171° . It was found more expeditious, however, to proceed in the following way. The alcoholic solution of the resin was treated with alcoholic soda and the solvent removed by distillation. The residual sodium salt was dissolved in water, and sufficient 10 per cent. aqueous sodium hydroxide added to cause a considerable precipitate to form. This mixture was then warmed on the water-bath until solution occurred. On cooling, a precipitate of the sodium salt slowly formed, which, when examined by aid of a lens, was found to consist of minute needles. This sodium salt can be recrystallised in the same way.

From this recrystallised salt the acid was then obtained by adding hydrochloric acid to its aqueous solution, filtering off the precipitate, and after washing and drying it, dissolving in alcohol and adding sufficient distilled water to render the solution faintly turbid. From this solution there separated in a few hours a colourless, crystalline substance, which, after recrystallising once or twice in the same manner, melted constantly at 171° .

The pure substance can also be prepared without the intervention of the sodium salt by taking the purified resin left after removal of the alcohol by distillation and distilling under 10—20 mm. pressure. Under these conditions, the residue distils easily and the temperature rises rapidly to 265° under 11 mm. pressure, and remains constant until the whole has passed over, condensing at first as a white, crystalline sublimate, and later, owing to the increasing temperature of the receiver, as a very viscous resin. A little care has to be exercised in carrying out this operation, as the solid acid is rather liable to block up the exit tube of the flask from which it is being distilled. The distillate obtained is at the ordinary temperature a vitreous, yellowish solid which can be left for months without showing signs of crystallisation. If, however, a little 70 per cent. alcohol be added to it, crystals immediately begin to form round the edges, and the whole mass becomes warm and crystallises rapidly. On recrystallisation, this acid melts at 171° , and is in every way similar to that obtained by the first-mentioned method. It crystallises in spreading rosettes of flat.

tened needles, is soluble in alcohol, ether, chloroform, or acetone, insoluble in water or petroleum, and slowly dissolves when warmed with aqueous alkali solutions. When a little is dissolved in a few drops of chloroform and about 1 c.c. of acetic anhydride added, the addition of a drop of strong sulphuric acid causes the formation of a transient pink coloration. This reaction is a convenient means of distinguishing the acid from abietic acid, which gives, under the same conditions, a deep purple colour fading into olive green.

The crystalline acid prepared in any of the three ways described is not optically active in alcoholic solution.

Combustions of the substance dried at 100° gave the following results:

0.1280 gave 0.374 CO_2 and 0.1083 H_2O . $\text{C} = 79.6$; $\text{H} = 9.3$.

0.1638 „ 0.4745 CO_2 „ 0.1413 H_2O . $\text{C} = 78.9$; $\text{H} = 9.5$.

$\text{C}_{20}\text{H}_{30}\text{O}_2$ requires $\text{C} = 79.4$; $\text{H} = 9.9$ per cent.

Combustions of the non-crystalline distillate were also made in order to ascertain whether this substance might not be the pimarinic anhydride which has been asserted to exist.

0.1647 gave 0.4792 CO_2 and 0.1497 H_2O . $\text{C} = 79.41$; $\text{H} = 9.96$.

$\text{C}_{40}\text{H}_{58}\text{O}_3$ requires $\text{C} = 81.9$; $\text{H} = 9.8$ per cent.

$\text{C}_{20}\text{H}_{30}\text{O}_2$ „ $\text{C} = 79.47$; $\text{H} = 9.9$ „

This result shows that the distillate is merely pimarinic acid in an amorphous form.

The basicity of the acid was determined by titration of the alcoholic solution of the acid with decinormal soda, using phenolphthalein as indicator. 0.0902 required 3.5 c.c. $N/10$ NaHO ; whence 40 grams NaHO neutralise 301 grams of acid. $\text{C}_{20}\text{H}_{30}\text{O}_2 = 302$.

Salts of Inactive Pimarinic Acid.—The sodium and potassium salts are easily obtained by boiling the acid with excess of solution of the alkali. On cooling, the salt crystallises out in microscopic needles.

The *silver* salt was prepared by the addition of silver nitrate solution to an aqueous solution of the sodium salt of *i*-pimarinic acid. It is an amorphous white powder which is only slowly affected by light, showing merely a slight purple coloration even after several weeks' exposure.

0.0445 gave 0.0117 Ag . $\text{Ag} = 26.2$.

0.1454 „ 0.0384 Ag . $\text{Ag} = 26.3$.

$\text{C}_{20}\text{H}_{29}\text{O}_2\text{Ag}$ requires $\text{Ag} = 26.4$ per cent.

Ethyl Ester.—When the silver salt of pimarinic acid is added to ethyl iodide, a deep purple-red solution is formed, which becomes colourless on addition of alcohol, silver iodide being precipitated. The residue

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left after removal of the solvent cannot be crystallised, but can be distilled at 280—285° under 11—12 mm. pressure. It is a slightly yellowish, hard resin.

Comparison of Abietic and Inactive Pimaric Acids.

As considerable difficulty has been found by previous workers in distinguishing between abietic and *d*- and *l*-pimaric acids, it was thought advisable to prepare specimens of abietic and *d*-pimaric acids for comparison with the acid obtained from sandarac resin.

Abietic acid was easily obtained by the solution of colophony, derived from *Pinus excelsa* grown in India, in 90 per cent. alcohol and the addition of sufficient water to render the solution turbid. After a few days, a large crop of colourless crystals was obtained. These were recrystallised in the same way, and the recrystallisation repeated until the substance melted constantly at 161° [the melting point of abietic acid is 152° (Mach), or 165° (Maly)]. The substance crystallises when pure in broad laminae, which are colourless and possess a brilliant lustre.

The sodium salt was prepared by neutralisation of an alcoholic solution of the acid with normal soda. To the liquid so obtained, sufficient normal soda solution was added to precipitate the sodium salt, which was then collected, dried, and recrystallised from dilute soda, forming masses of minute needles.

The silver salt was prepared from the latter by double decomposition in the usual manner. It is a white, amorphous substance. On analysis, it gave the following result:

0.0564 gave 0.0158 Ag. Ag = 28.01.

$C_{19}H_{27}O_2Ag$ requires Ag = 27.4 per cent.

$C_{20}H_{29}O_2Ag$ „ Ag = 26.22 „

As has already been pointed out, Mach, in his recent investigation of the pine resins, showed that it was not possible to isolate *d*-pimaric acid from the “galipot” or French colophony of commerce. Recourse was therefore had in the present instance to Burgundy pitch, which is generally supposed to be made from the oleo-resin of *Pinus maritima*, but from three specimens examined only one and the same acid melting at 161°, identical in all respects with that obtained from the resin of *Pinus excelsa*, could be isolated; thus the silver salt, prepared as already described, gave the following result on analysis:

0.046 gave 0.0126 Ag. Ag = 27.39.

$C_{19}H_{27}O_2Ag$ requires Ag = 27.4 per cent.

$C_{20}H_{29}O_2Ag$ „ Ag = 26.4 „

The attempt to prepare *d*-pimaric acid was therefore abandoned.

The differences between the pimarinic acid isolated from sandarac and abietic acid may be grouped thus :—

Inactive pimarinic acid, $C_{20}H_{30}O_2$.	Abietic acid, $C_{19}H_{28}O_2$.
<p>Melts at 171°. Optically inactive. Crystallises in needles. A solution in chloroform and acetic anhydride gives a pink colour with concentrated sulphuric acid.</p> <p>Distils unchanged at 265° under 11 mm. pressure.</p>	<p>Melts at 161°. $[\alpha]_D + 66^\circ$. Crystallises in laminae. A solution in chloroform and acetic anhydride gives a violet colour fading to olive green with concentrated sulphuric acid.</p> <p>Distils unchanged at 259° under 20 mm. pressure.</p>

Action of Bromine.—When a chloroform solution of bromine is gradually added to pimarinic acid dissolved in the same solvent, the bromine is absorbed, and no hydrogen bromide is formed until the equivalent of two atoms of bromine per molecule has been added. On removing the chloroform by spontaneous evaporation, an oily substance is left, which, when dissolved in hot alcohol, deposits a colourless, granular bromine derivative on cooling. This substance has so far resisted all attempts to crystallise it.

The acid is not attacked by fused potash. After heating for 20 minutes at 200° , a considerable proportion of the acid was recovered unchanged, whilst only resinous products were formed from the remainder.

Action of Hydriodic Acid.—When the acid is heated in sealed tubes at 200 – 210° for 4 hours with excess of fuming hydriodic acid, it is completely reduced, forming an oily hydrocarbon. The product was made alkaline, when a small amount of iodoform was precipitated. The mixture was then shaken with ether, the ethereal solution separated, dried over solid potash, and the solvent removed by distillation. The brownish, oily residue was then distilled under 11–12 mm. pressure, and the fraction boiling between 170° and 190° , constituting about 90 per cent. of the whole, collected. This was then distilled over sodium, and after repeating this treatment twice, the oil boiled almost entirely between 180° and 185° under 11 mm. pressure. It forms a faintly yellow, oily liquid with a bluish fluorescence and has an odour recalling that of the crude higher paraffins. Its density at $15^\circ/15^\circ$ is 0.967. It is optically inactive, rapidly resinifies on exposure to air, decolorises bromine in ethereal solution, and does not absorb hydrogen chloride. It decomposes slightly when distilled under atmospheric pressure.

On combustion, the following result was obtained :

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0.1237 gave 0.406 CO_2 and 0.128 H_2O . $\text{C} = 88.9$; $\text{H} = 11.5$.

$\text{C}_{20}\text{H}_{32}$ requires $\text{C} = 88.3$; $\text{H} = 11.7$ per cent.

The refractive index for sodium light was determined, using a small, hollow prism of refracting angle $61^\circ 25'$. The angle of minimum deviation was found as the mean of ten observations to be $40^\circ 53'$, whence $\mu = 1.5254$.

This hydrocarbon is apparently identical or isomeric with that obtained by Liebermann, Haller, and Vesterberg (*loc. cit.*), by reduction of the *d*-pimaric acid of "Bordeaux colophony" with hydriodic acid. It was suggested by Liebermann, who assigned to it the formula $\text{C}_{20}\text{H}_{32}$ or $\text{C}_{20}\text{H}_{34}$, that it was probably identical with the colophene (or colophene dihydride) obtained by Deville (*loc. cit.*) by the action of concentrated sulphuric acid on turpentine. For this substance, the name "dicamphene," as more suitably indicating its origin, has since been suggested by Armstrong and Tilden (Trans., 1879, 35, 733). A specimen of "colophene" was prepared by the addition of strong sulphuric acid to turpentine in the proportion of 1 : 5. The volatile hydrocarbons were removed, as recommended by Armstrong and Tilden, by steam distillation, and the residual emulsion shaken with ether to remove the colophene. This solution was dried, the solvent removed in the usual way, and the residue distilled under 10—14 mm. pressure. A considerable amount of hydrocarbon came over below 100° ; the boiling point then rose rapidly to 190° and remained constant.

The portion boiling in the neighbourhood of 190° was collected and redistilled over metallic sodium, when it boiled constantly at 190° under 12 mm. pressure. This distillate is, however, not quite pure, as it always has a slight odour of camphene and of some sulphur compounds, which even repeated distillation over sodium fails to remove.

On redistillation, a few drops of distillate were obtained before the temperature became constant (206° under 35 mm. pressure), but the amount was not more than 0.1 per cent. of the whole. The observations of Armstrong and Tilden (*loc. cit.*) seem to indicate that this substance cannot be distilled even under diminished pressure, but there seems to be no difficulty in so distilling it if the pressure be sufficiently diminished. The purified substance is a viscous, slightly yellowish oil, having a camphoraceous odour which becomes somewhat pungent when warmed. It decomposes slightly when heated under the ordinary pressure, but is not decomposed even at 150° in sealed tubes. Its density at $15^\circ/15^\circ$ is 0.931.

The refractive index for sodium light was determined, using a small, hollow prism of refracting angle $61^\circ 25'$. The angle of minimum deviation was found as the mean of ten observations to be $40^\circ 49'$, whence $\mu = 1.5136$.

A comparison of the properties of colophene and the hydrocarbon obtained by the reduction of pimaric acid shows clearly that these two substances are not identical.

	Relative density.	Refractive index.	B. p. under 11 mm. pressure.
Colophene	0.931	1.5136	190°
Sandarac hydrocarbon.....	0.967	1.5254	180—185

Further, colophene is only slightly volatile with steam, whilst the sandarac hydrocarbon can easily be distilled in this way. The new hydrocarbon is also fluorescent, whilst colophene does not possess this property.

Action of Nitric Acid.—The acid is but slightly attacked, except by hot concentrated nitric acid, when it is converted into oxalic acid.

Oxidation by Potassium Permanganate.—When solution of potassium permanganate is added to an aqueous solution of the sodium salt of pimaric acid, decolorisation quickly occurs. The addition of the reagent was continued until the tint remained permanent for 4 hours. The solution was then filtered from manganese dioxide, and made acid by the addition of dilute sulphuric acid. A considerable amount of resin was precipitated containing some unchanged acid; this was filtered, and the filtrate distilled with steam. The distillate was distinctly acid. It was neutralised by addition of caustic soda solution evaporated to a small bulk, and silver nitrate solution was added to it. After a few minutes, a crystalline precipitate formed. This was collected and analysed, with the following result:

0.0105 gave 0.0067 Ag. $\text{Ag} = 63.8$.

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$ requires $\text{Ag} = 64.4$ per cent.

The volatile acid was therefore acetic acid.

The liquid, after distillation with steam, was shaken out with ether, the ethereal solution separated, dried over calcium chloride, and the solvent distilled off, leaving an oily residue, which, after standing for several days with occasional stirring, deposited a small quantity of minute needles. The substances melted at 260° , gave a buff-coloured bromo-compound with bromine water, and its aqueous solution was acid to litmus paper. A sufficient quantity of this substance has not yet been obtained for its complete identification, but its properties are similar to those of trimellitic acid (m. p. 262°), which has already been found to occur among the oxidation products of crude pine resin.

Callitrolic Acid.

This is the name given by Tschirch and Balzer to the acid whose potassium salt is soluble in excess of an aqueous solution of potash, but it is used in this paper to denote the second resin acid of sandarac.

When the strongly alkaline solution of the potassium salt of callitrolic acid, obtained during the isolation of pimaric acid, is acidified with concentrated hydrochloric acid, almost the whole of the resin precipitated is insoluble in alcohol. This precipitate was boiled with alcohol until nothing more dissolved, and then treated with alcoholic potash, in which it dissolved completely. The solvent was removed by distillation, the residue dissolved in water, and more potash added. It was found that by slowly concentrating this liquid the potassium salt could be precipitated in fractions, the later fractions being nearly free from colour. These were collected, dried, and the acid regenerated by addition of acetic acid. Many attempts were made to crystallise this substance by addition of water, benzene, petroleum, &c., to its solutions in alcohol and ether, by fractional precipitation, and by purification through the lead salt, but to no purpose.

Attention was therefore turned to the preparation of derivatives, in the hope that they might be more easily crystallised, and eventually a crystalline sodium salt was obtained by dissolving the acid in absolute alcohol, and adding to that solution alcohol in which metallic sodium had been dissolved. In this way, a precipitate of the sodium salt was obtained in the form of microscopic needles. If, however, any attempt was made to remove and dry this salt, it absorbed water and formed a transparent jelly, even if the whole mixture was poured on a porous tile and the latter at once placed in a vacuum desiccator over calcium chloride. Experiments made with other salts were no more satisfactory, the potassium and ammonium salts being equally deliquescent, whilst salts of the other common metals are amorphous.

Action of Acids on Aqueous Solutions of the Alkali Salts of Callitrolic Acid.—When acids are added to aqueous solutions of the alkali salts of callitrolic acid, this acid is set free, forming a yellowish powder which may be either completely or partially insoluble in alcohol, depending on the concentrations of the acid used for the precipitation. Thus, if strong hydrochloric acid be used, the precipitate is almost insoluble in absolute alcohol, whilst if only a 10 per cent. solution of hydrochloric acid be added, a mixture of a soluble and an insoluble resin is obtained, and if acetic acid be used as the precipitating agent, the resin obtained is almost completely soluble. The *insoluble* resin

dissolves in alcoholic potash, and from this solution there can be regenerated by acetic acid a resin *soluble* in alcohol. The obvious explanation of this behaviour is, that callitrolic acid is a hydroxy-acid, which in the presence of mineral acids forms a *lactone*.

This lactone is insoluble in alcohol, acetone, ether, chloroform, benzene, or petroleum; but dissolves in hot glacial acetic acid, from which it is deposited on cooling as a granular powder, which occasionally assumes a somewhat crystalline appearance, but has never been obtained in an undoubtedly crystalline condition. If the lactone be added to concentrated alcoholic solution of inactive pimaric acid, it passes into solution, and, if the latter be diluted with alcohol, is reprecipitated as a white, granular powder.

As no crystalline derivative of callitrolic acid, except the unsatisfactory sodium salt, could be obtained, it was thought advisable to prepare specimens of the insoluble lactone in various ways, and submit these to analysis. These specimens of lactone were prepared: (a) by precipitation by concentrated hydrochloric acid from a specimen of freshly prepared crystalline sodium salt; (b) by precipitation from alcoholic solution of pimaric acid, the precipitate being washed with absolute alcohol; (c) by precipitation from hot glacial acetic acid solutions.

On combustion, the following results were obtained:

- (a) 0.2065 gave 0.5802 CO₂ and 0.1747 H₂O. C = 76.6; H = 9.3.
 (b) 0.2505 „ 0.6969 CO₂ „ 0.2140 H₂O. C = 76.09; H = 9.50.
 0.1600 „ 0.4462 CO₂ „ 0.1325 H₂O. C = 76.06; H = 9.20.
 (c) 0.2830 „ 0.7899 CO₂ „ 0.2415 H₂O. C = 76.14; H = 9.40.
 0.1798 „ 0.5080 CO₂ „ 0.1490 H₂O. C = 77.03; H = 9.18.
 C₃₀H₄₆O₄ requires C = 76.6; H = 9.7 per cent.

The composition of callitrolic acid should therefore be represented by the formula C₃₀H₄₈O₅, which is confirmed by a large number of analyses of the silver salt prepared from the following specimens of the lactone through the intervention of the sodium and potassium salts: (i) From lactone deposited from alcoholic solutions of pimaric acid; (ii) by solution of lactone, from acetic acid, in alcoholic potash, and precipitation with silver nitrate; (iii) by solution of lactone, from acetic acid, in alcoholic potash and fractionation by addition of excess of aqueous potash, the fractions being converted into silver salt:

- (i) 0.2322 gave 0.0377 Ag. Ag = 18.02.
 (ii) 0.5540 „ 0.0981 Ag. Ag = 17.7.
 0.4132 „ 0.0730 Ag. Ag = 17.66.
 (iii) 0.1061 „ 0.0200 Ag. Ag = 18.09.
 0.1007 „ 0.0180 Ag. Ag = 17.80.
 C₃₀H₄₇O₅Ag requires Ag = 18.14 per cent.

Although, therefore, the composition of callitrolic acid cannot at present be definitely asserted to be that represented by the formula $C_{30}H_{48}O_5$, yet it is improbable that it is far removed from this.

The acid and its lactone are not acted on by fused potash and hot fuming nitric acid. With the latter reagent, the resin agglomerates into a semi-solid mass, and shows no sign of solution, even after warming for several days on the water-bath. An aqueous solution of the sodium salt slowly decolorises potassium permanganate, but the action soon stops unless the solution is kept hot. This is the only reaction, so far found, which seems likely to afford a method of attacking this substance. When the acid or lactone is heated with hydriodic acid in Zeisel's apparatus, no methyl iodide is formed. The acid and its lactone both react with acetic and benzoic anhydrides, with the formation of insoluble acyl compounds, which have not yet been examined.

Heating in a Vacuum.—When heated, callitrolic acid is completely decomposed, giving off carbon dioxide and an oily hydrocarbon, and leaving a hard, pitch-like residue. It was found that this operation gave a better yield of hydrocarbon when carried out under diminished pressure (360 mm.). The distillate consists of a viscous, oily liquid containing a little water, and having an odour of acetic acid. It was dissolved in ether, and the ethereal solution shaken out with dilute potash. The ethereal portion was separated, washed with water, dried over calcium chloride, and the solvent distilled off. The residue was then distilled, almost the whole passing over from 230—285°. On analysis at this stage, the oil was found to contain less than 1 per cent. of oxygen, so that it was evidently a hydrocarbon. Its further purification was therefore conducted by distillation over metallic sodium. The final product, purified in this way, boiled from 270—280°, was almost colourless when freshly prepared, but resinified slightly and became greenish on keeping, and had a faint odour of peppermint, especially when heated. In appearance and odour it closely resembled the diterpene naturally occurring in the plant, and like it gave a purple coloration when concentrated sulphuric acid was added to its solution in acetic acid. Its density at 15°/15° was 0.9303.

The hydrocarbon is optically active. Determinations of its specific rotation for sodium light, using a 100 mm. tube, gave as the mean of ten concordant determinations $+36^\circ$, whence $[\alpha]_D +38^\circ 42'$.

The refractive index was determined in a hollow prism of refracting angle $61^\circ 25'$; the minimum angle of deviation for sodium light was found to be $40^\circ 47'$, whence $\mu = 1.5238$.

Combustions of this hydrocarbon, freshly distilled over metallic sodium, gave the following results :

0.1581 gave 0.510 CO_2 and 0.1615 H_2O . $\text{C} = 87.9$; $\text{H} = 11.1$.

0.2243 „ 0.7269 CO_2 „ 0.2270 H_2O . $\text{C} = 88.3$; $\text{H} = 11.2$.

$\text{C}_{20}\text{H}_{32}$ requires $\text{C} = 88.23$; $\text{H} = 11.77$ per cent.

The following tabular statement of the properties of the diterpene occurring in the plant and that obtained by destructive distillation of callitrolic acid shows clearly that they are identical:

	B. p.	Rel. dens.	Specific rotation.	Composition.	Refractive index.
Diterpene occurring in resin	260—280°	0.9386	+55°	$\text{C}_{20}\text{H}_{32}$	1.5215
Diterpene ex-callitrolic acid	270—280	0.9303	+38°42'	$\text{C}_{20}\text{H}_{32}$	1.5238

The difference in the optical rotation of the two substances is to be accounted for by the production of both dextro- and lævo-forms during the destructive distillation of the callitrolic acid.

Resin of Callitris Verrucosa.

The resin of this plant has been examined in the way already described in detail in the foregoing part of this paper. It contains pinene and a small quantity of a constituent of higher boiling point, of which sufficient could not be obtained for examination from the small amount of resin available. The resin itself is composed of inactive pimarinic and callitrolic acids, the former being present in much larger quantity than in the case of the resin of *Callitris quadrivalvis*. The softness of this resin is due to the greater proportion of pinene contained in it which, perhaps, also to some extent affects the rapidity of its solubility in alcohol.

Volatile Resins.

Although it is known that abietic acid is volatile when heated in a vacuum, this substance having been isolated by Kelbe from the distillation products of colophony (*Ber.*, 1880, 13, 888), and that *d*-pimaric acid can be distilled unchanged in a vacuum (Vesterberg, *loc. cit.*), yet this method has been but little used by investigators for the isolation of resin constituents, the only case of its application (which seems to have been accidental) being the preparation of cannabinal from the resin of Indian hemp by Messrs. Wood, Spivey, and Easterfield (*Trans.*, 1899, 75, 20). During the course of the present work it was found that distillation of sandarac under reduced pressure was a very con-

venient way of obtaining inactive pimaric acid. The resin was broken into small pieces and placed in a Jena distilling flask having another similar flask attached to its side arm in the usual way. The flasks were then rendered vacuous (10—12 mm. pressure) and the resin heated by a Bunsen burner. At first a little water came over, and the resin melted and began to froth. The frothing was easily controlled by the use of a glass T-piece, inserted between the pump and the flasks, having one arm closed by a piece of rubber tubing and a spring clip, so that the pressure in the flasks could be suddenly increased at will by opening the clip. After a time, the volatile oil began to distil over, the thermometer gradually rising to about 160°. The receiver was changed at this stage, and a fraction up to about 240° collected. This was usually viscous when cold, and was found to be a mixture of pimaric acid and diterpene. The receiver was again changed and a fraction up to 300° collected. This was almost pure pimaric acid, and on redistillation usually gave a large fraction boiling at 260° under 15 mm. pressure which, on solution in alcohol and addition of a little water, could be obtained in a crystalline condition (m. p. 171°). In this process, the callitrolic acid suffers decomposition, and so a large yield of diterpene is obtained in the earlier fractions. This can be purified by shaking the ethereal solution of the fraction with potash to remove pimaric acid, and rectification as already described over metallic sodium.

Among other resins which on distillation under diminished pressure give constituents of constant boiling point are mastic, myrrh, and Indian frankincense. The application of this process could no doubt be extended with great advantage to the investigation of this class of substances, about the chemistry of which so little is known owing to the difficulty of isolating well-defined products from them.

Summary and Conclusions.

Briefly stated, the principal results obtained in the course of the present investigation are as follows.

It is shown that the crude resin consists of a mixture of resin acids and volatile hydrocarbons. The latter have been separated into a diterpene and *d*-pinene.

Two acids have been isolated from sandarac resin. One of these has the composition represented by the formula $C_{20}H_{30}O_2$. It is not identical with abietic acid but is isomeric with Vesterberg's *d*-pimaric acid, and as it differs from the latter in being optically inactive, it is proposed to call it *i*-pimaric acid.

The remaining acid of the resin is probably the chief constituent of Tschirch and Balzer's callitrolic acid, so that the latter name may

conveniently be retained for it. It yields a lactone of the composition $C_{30}H_{46}O_4$, from which it may be inferred that the composition of the acid is represented by the formula $C_{30}H_{48}O_5$. This lactone, although insoluble in all the usual solvents except boiling acetic acid, is dissolved readily by alcoholic solutions of *i*-pimaric acid, and is reprecipitated from such solutions by the addition of alcohol. This phenomenon has already been observed by Johnston (*loc. cit.*), who found that a strong varnish of crude sandarac, made with alcohol, deposited the A resin on dilution with more alcohol. This experiment has been repeated, and the A resin of Johnston has been found to be identical with the lactone of callitrolic acid.

The resin of *Callitris verrucosa* has also been examined and found to contain *d*-pinene, and the two resin acids already obtained from common sandarac.

It should be pointed out that in many particulars the observations now recorded do not confirm those of Tschirch and Balzer. The sandaracolic acid of these authors was probably impure *i*-pimaric acid, and could not have given methyl iodide when heated with hydriodic acid, since no constituent of sandarac resin behaves in this way, as has also been shown by Gregor and Bamberger (*Oesterr. Chem. Zeit.*, 1898, 1, 8), who obtained no methyl iodide when the crude resin was heated in Zeisel's apparatus with hydriodic acid. The formation of acetyl and benzoyl derivatives from sandaracolic acid (impure *i*-pimaric acid) is also inexplicable, except on the assumption that it contained much callitrolic acid, which is hardly probable if, as the authors say, their sandaracolic acid was distinctly crystalline. Tschirch and Balzer further failed to observe the formation of the insoluble lactone when attempts are made to regenerate callitrolic acid from aqueous solutions of its alkali salts by addition of mineral acids. The formulæ now proposed for the acid constituents of sandarac resin also differ considerably from those proposed by these authors.

The experimental results obtained in the course of this work, although not yet sufficiently definite and extensive to enable a constitutional formula to be assigned to *i*-pimaric acid, lend support to the view generally held that the resin acids of the *Coniferae* are produced by the condensation and oxidation of terpenes; a view to which concrete expression has been given in the constitutional formulæ assigned by Bruylants and by Bischoff and Nästvogel to resin acids of the composition $C_{20}H_{30}O_2$, to which attention has already been drawn in the historical introduction to the present paper.

This investigation has been carried out in the laboratories of the Scientific Department of the Imperial Institute, and I desire to express

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my warmest thanks to Professor Dunstan both for the suggestion that I should undertake this work and for the valuable help he has given me during its pursuit.

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