CCCLXIV.—*Examination of the Volatile Oils from* Xanthorrhœa arborea, X. hastilis, *and* X. reflexa.

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Rennie, Cooke, and Finlayson (J., 1920, **117**, 338) have described the examination of two species of *Xanthorrhœa* resin from Kangaroo Island, and of the resin of *X. Preissii* from West Australia. The present paper is an account of the examination of the resins of two other species from New South Wales, *viz.*, *X. arborea* and *X. hastilis*, and of *X. reflexa* (a species closely resembling *X. Preissii*) from West Australia.

In each case the volatile oil was obtained, in the way previously described, by the distillation of an alkaline solution of the resin with steam and was separated into phenolic and non-phenolic portions by shaking it with a solution of sodium hydroxide.

Examination of X. arborea.—*Volatile oil.* The specimen of resin used was fairly clean and comparatively free from husks and gravel—the individual flakes of resin were dark brownish-red and nearly opaque.

The oil, the yield of which amounted to about 1%, was dark brown and of agreeable spicy odour recalling that of the oil from *X. Tateana.*

The non-phenolic portion from 15 g. of oil amounted to 4·5 g., was very viscous and dark brown, and appeared to contain all the sweet-smelling constituents of the original oil. When an attempt was made to distil it at 18 mm. the liquid frothed excessively owing to the presence of sticky, resinous, scarcely volatile substances, and these were therefore removed by steam distillation. The light yellow rectified oil recovered from this distillate (now reduced to 2·5 g.) distilled at 115—190°/18 mm. and appeared to contain a number of substances about which very little could be learned owing to the small quantity of material available; the odour, however, was indistinguishable from that of the corresponding fractions of the oils from *X. Tateana* and the yellow resin from Kangaroo Island (*loc. cit.*).

The 10·5 g. of phenols, also dark brown, when fractionated at 18 mm., gave 7·5 g. from 155—165° and about 1 g. from 165—190°, leaving 1·5 g. of a dark brown resinous residue.

The first two fractions slowly solidified almost completely, and from them, by recrystallisation from dilute alcohol, large proportions of pure pæonol and hydroxypæonol of m. p. 49° and 80°, respectively, were obtained.

The approximate composition of the oil from this species is therefore : Pæonol 50%, hydroxypæonol 6·5%, non-phenolic substances of b. p. 115—190°/18 mm., including the fragrant principle of the resin, 17%, and dark-coloured resinous substances, partly soluble and partly insoluble in alkali, and presumably formed by oxidation and polymerisation of other constituents, subsequent to the first distillation, 26·5% (diff.).

Acids. The acids, which in the species previously examined appeared to be loosely attached to the complex resin molecule and were easily split off by a short digestion with dilute alkali, were again tested for in the present instance, but without success. The method used was identical with that previously described (*loc. cit.*), but on evaporation of the ethereal extract only a very small quantity of a dark oily substance was obtained from which neither *p*-hydroxybenzaldehyde, *p*-coumaric acid, nor any other crystalline acid could be separated.

Examination of X. hastilis.—The specimen of the resin of this species was much less homogeneous than that of *X. arborea*, and the material insoluble in alcohol—husks, sand, etc.—amounted to 25% of the whole. The individual flakes of resin varied in colour from a dull mustard to a brownish-yellow.

Volatile oil. The yield of oil calculated on the pure resin taken was 1·56%. It was a pale yellow liquid of pleasant odour differing entirely from that of *X. arborea.*

Phenols. 23·5 G. of oil, on treatment with alkali, yielded 1·16 g. of brown liquid phenols which, even when cooled strongly and seeded with pæonol and hydroxypæonol, showed no signs of crystallisation.

The alcoholic solution gave with ferric chloride a reddish-brown coloration, and with cold nitric acid a dull green coloration developed which changed rapidly to yellow on warming. Pæonol and hydroxypæonol appeared to be entirely absent, and in this respect the resin differs from all others previously examined.

Non-phenols. After thorough drying over anhydrous potassium carbonate the non-phenols were carefully fractionated under 18 mm. After three series the following fractions were obtained : (I) up to 130°, 3·0 g.; (II) 130—140°, 1·5 g.; (III) 140—150°, 10·0 g. The dark sticky residue weighed 6—7 g.

Fraction I had a very pleasant rose-like smell, changing on shaking with dilute chromic acid to the penetrating smell of citronellal, and on acetylation acetates were formed closely resembling citronellyl acetate in odour—so that the presence of citronellol seemed fairly certain.

In an attempt to prove the presence of this alcohol, the acid phthalic esters were prepared and converted into the corresponding silver salts; from these, by repeated crystallisation from boiling methyl alcohol, a fraction was obtained of m. p. 123—125° which contained 27·55% Ag as against 26·23% required for the citronellyl compound, 26·4% for the geranyl, and 27·76% for the cinnamyl phthalate.

Fraction III, after several redistillations under low pressure, and after long standing, solidified almost completely, and when freed from oily impurities by long and heavy pressure between blotting paper, the solid had m. p. 32—33° and b. p. 142—144°/18 mm. and 126—128°/5—7 mm. It was proved to be cinnamyl alcohol by its behaviour on oxidation, by the preparation of the dibromide of m. p. 72—73°, and by comparison with an authentic sample.

Fraction II also consisted largely of cinnamyl alcohol contaminated with small quantities of the lower-boiling, fragrant alcohols.

The oil from this species therefore approximately consists of fragrant, low-boiling alcohols 8% (probably largely citronellol), cinnamyl alcohol 53%, phenols 5%, and resinification products.

The resin was examined for acids in the same way as in previous cases, but oily, indefinite substances only were obtained, and these in small quantity.

Examination of X. reflexa.—*Volatile oil.* The specimen of resin examined was a very homogeneous one, picked out from 20 lb. of the rough material and consisting of large tears free from husk and woody matter. It differed from the resin of *X. Preissii*, with which it is botanically closely associated, in its much darker colour, which, however, is less noticeable in powdered specimens.

The yield of oil was 6·86%. It was dark brown and of pleasant smell. 68·59 G. of it were treated with alkali and separated into a phenolic and a non-phenolic portion.

Phenolic portion. The portion (48 g.) soluble in alkali was systematically fractionated at a pressure of 18 mm., with the following results: (1) up to 150°, 2·0 g.; (2) 150—160°, 41·0 g.; (3) 160—175°, 1·75 g.; (4) 175—185°, 1·25 g. On standing, fractions 1 and 3 solidified partly, 2 and 4 completely.

Fraction 1, on prolonged pressure between blotting-paper, gave 1 g. of crystalline pæonol. The oily portion recovered from the paper by extraction with ether, and still containing a small quantity of pæonol, was a phenol of lower boiling point with a creosote-like smell. Its colour reaction with ferric chloride was identical with that of pæonol and it yielded a benzoate readily, which, however, refused to crystallise. The quantity was insufficient for further examination.

Fraction 2, on recrystallisation from alcohol, yielded almost its own weight of pure pæonol, m. p. 49°.

Fraction 4 similarly yielded hydroxypæonol, and the intermediate fraction consisted of a mixture of the two compounds, pæonol predominating.

Non-phenolic portion. After removal of the solvent from the benzene washings from the treatment of the original oil with alkali, 19 g. of dark brown, aromatic-smelling, non-phenols were obtained which on fractionation at 18 mm. gave the following results: (1) up to 100°, 2·25 g.; (2) 100—200°, 2·20 g.; (3) 200—210°, 11·75 g. The residue weighed 1·5 g.

Fraction 1 consisted essentially of benzaldehyde, which was identified by oxidation to benzoic acid on exposure to air and by preparation of the phenylhydrazone of m. p. 155°. The smell was modified somewhat by the presence of a small quantity of the ketone mentioned below.

Fraction 2 consisted of a pale yellow, highly refractive liquid of powerful aromatic smell recalling strongly that of some acacia blossoms. Small quantities of benzaldehyde and of the high-boiling compound of fraction (3) were present, but the chief constituent appeared to be a saturated aromatic ketone, yielding a pale yellow phenylhydrazone of m. p. 114° and a liquid oxime. On oxidation by prolonged boiling with 5% chromic acid mixture, a greasy neutral product was formed, together with a small yield of a mixture of crystalline acids, a partial separation of which was effected by steam distillation. From the non-volatile portion, by repeated crystallisation from dilute alcohol, long, pale yellow needles of m. p. 180·5° (corr.) were obtained, which, when heated with soda-lime, developed an unmistakable smell of anisole—a mixture of equal parts of this acid and of a specimen of anisic acid melted at 183°. The acid volatile with steam was not homogeneous and was obtained in very small quantity only: it melted indefinitely at 140—145° and gave a yellow insoluble ferric salt. The quantity of the ketone available was insufficient for further work.

Fraction 3 solidified completely on standing and after recrystallisation from alcohol gave 10 g. of white, crystalline material, m. p. 68—69°, $[\alpha]_{D}^{13^{\circ}}$ + 55·57° (in 10% benzene solution). The substance was identical with that previously isolated from the corresponding fraction of *X. Preissii*.

The approximate composition of the volatile oil from *X. reflexa* is therefore pæonol, 62·8%; hydroxypæonol, 2·9%; phenols of lower boiling point than the above, 1·5%; benzaldehyde, 3·2%; an aromatic ketone containing one *p*-methoxyphenyl group, 3%;

the compound of m. p. 68—69° previously isolated from *X. Preissii*, 17·5%; resinous residues, loss, and undetermined, 9·1%.

The compound of m. p. 68—69°, to which the formula $C_{13}H_{12}O_2$ was provisionally ascribed, has now been found to possess optical activity, a fact which was previously overlooked. Although many analyses have been made, the figures obtained are not decisive; they appear, however, in the main to indicate the formula $C_{14}H_{14}O_2$ rather than $C_{13}H_{12}O_2$. The substance is extremely stable and so far no derivatives have been prepared which throw any light on its relationships. Experiments are being undertaken to accumulate a larger quantity than has yet been available with a view to further examination.

The products from *X. Preissii* and *X. reflexa*, which are botanically closely allied, are very similar chemically and differ from those of any other species in containing the unidentified substance above referred to.

In conclusion I desire to thank Professor E. H. Rennie, who has maintained a most helpful interest in this work, and also Mr. F. K. Carter, B.Sc., and Mr. J. G. Wood, B.Sc., who gave valuable assistance.

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[*Received, May* 11*th*, 1926.]