NOTES.

Pyrolysis of Xanthopinacol and Related Compounds. By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

IN view of the ready decomposition of xanthopinacol by light (Schönberg and Mustafa, this vol., p. 67) its thermal decomposition is of interest. Bergmann and Schuchardt (*Annalen*, 1931, **487**, 225), decomposing it in' toluene or chlorobenzene, isolated only xanthone. We carried out its thermal decomposition under conditions which allowed the preliminary products to be protected from further pyrolysis, and obtained xanthone together with a little xanthen and water. We believe that the thermal decomposition of xanthopinacol proceeds like that of benzopinacol, which yields benzophenone and benzhydrol. Benzhydrol, however, is comparatively stable thermally (Nef, *Annalen*, 1897, **298**, 235), whereas xanthhydrol very readily yields dixanthhydryl ether and water at 150—175° (Kny-Jones and Ward, J., 1930, 535) and the ether is readily decomposed into xanthen and xanthone at higher temperatures.

Corresponding results may be expected from the pyrolysis of pinacols when the decomposition is carried out at temperatures such that the secondary alcohol forms the corresponding ether, which in turn decomposes into the corresponding ketone and methane derivative. The formation of thioxanthen and thioxanthone from thioxanthhydrol at 120—130°, described by Finzi (*Gazzetta*, 1932, **62**, 211) and confirmed by us, may be explained on this basis, as the ether of thioxanthhydrol was not isolated. We obtained also dithiodïxanthylen, $S{<}^{C_6H_4}_{C_6H_4}{>}C{:}C{<}^{C_6H_4}_{C_6H_4}{>}S$.

Action of Heat on Xanthhydrol.—While dry carbon dioxide was passing through the apparatus, xanthhydrol (2 g. was heated (bath at 160°) for 2 hours in a tube (A), 25 cm. high, connected by a bent tube to a similar tube (B) containing water, externally cooled. The drops of liquid that collected in the bent tube were shown to be water by the rapid formation of a blue colour with anhydrous copper sulphate. The temperature was then kept at 200° for 20 minutes; a colourless sublimate appeared on the walls of the tube (A) and, on cooling, a pale yellow crystalline residue was left at the bottom. The sublimate, extracted with light petroleum (b. p. 30—50°) and crystallised from methyl alcohol, was shown to be xanthen by m. p. and mixed m. p. The residue crystallised from hot petroleum (b. p. 100—150°) in almost colourless needles and was proved to be xanthone (m. p. and mixed m. p.; blue fluorescence with sulphuric acid).

Action of Heat on Dixanthhydryl Ether.—The ether (5 g.) was heated (bath at 250°) in the apparatus described above; the vapours evolved condensed in the tube (B). The solid in tube (B) was steam-distilled and an ethereal extract of the distillate was dried over anhydrous sodium sulphate and evaporated in a vacuum; colourless crystals of xanthen (m. p. and mixed m. p.) were obtained. The solid in the tube (A), on steam-distillation, gave xanthen and xanthone, which were separated by extraction with hot light petroleum (b. p. 30—50°), in which xanthen is soluble; xanthone was crystallised from hot absolute alcohol and identified as above.

Action of Heat on Xanthopinacol.—(a) Xanthopinacol (5 g.) was heated as in the previous experiments (bath temp. 270°). Xanthen (Found : C, 85·6; H, 5·4. Calc. for $C_{13}H_{10}O$: C, 85·7; H, 5·4%) and xanthone were isolated.

(b) *Detection of water.* The pinacol was placed in a flask carrying a side arm containing two boats filled with anhydrous copper sulphate. The flask was sealed at the neck and evacuated through the side arm (the boats meanwhile being heated to drive out the last trace of moisture), which was then sealed. The apparatus was heated (bath at about 300°) for ½ hour and allowed to cool for 24 hours. The surface of the anhydrous copper sulphate had turned blue, indicating the formation of water. The neck of the flask was filled with crystals of xanthen and xanthone.

Action of Heat on Thioxanthhydrol.—Thioxanthhydrol (2 g.) (Meyer, *Ber.*, 1909, **42**, 1135) was heated at 120—130° (bath temp.) in a pyrex glass tube in a stream of carbon dioxide for 1 hour, a colourless crystalline sublimate being formed. From the product, light petroleum (b. p. 30—50°) extracted thioxanthen (m. p. and mixed m. p.). The residue was extracted with sufficient glacial acetic acid to dissolve the thioxanthone (m. p. and mixed m. p.; colour

reaction with sulphuric acid), leaving a solid which separated from hot xylene in fine colourless crystals of dithiodixanthylen, m. p. above 330°, which gave a blue fluorescence in the solid state (Found : C, 78·9; H, 4·6; S, 16·1. Calc. for $C_{26}H_{16}S_2$: C, 79·5; H, 4·1; S, 16·3%).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, February 3rd*, 1944.]

Geranylamine. By D. A. SUTTON.

THE published method of preparation of geranylamine hydrochloride has been re-examined with the object of obtaining homogeneous crystals suitable for use in *X*-ray studies of polyisoprenic materials. A preliminary account of the *X*-ray structure of this salt has recently been published from this laboratory (see Bateman and Jeffrey, *Nature*, 1943, **152**, 446). Forster and Cardwell prepared geranylamine from geranyl chloride (J., 1913, **103**, 1338), and converted it, by the action of dry hydrogen chloride in ethereal solution, into the hydrochloride, which darkened at 100° and melted at 120° and has since been considered (Beilstein, supplementary volume 4, p. 398) to be possibly a mixture of $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}NH_3Cl$ (I) and $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}NH_3Cl$ (II).

Geranylamine hydrochloride was prepared in the present work in the following way : Commercial geraniol was purified through its calcium chloride compound, and the regenerated alcohol (117 g.) converted into geranyl chloride by the action of phosphorus trichloride (78·4 g.) in petrol solution (see Farmer and Sutton, J., 1943, 116). The middle fraction of the product (74 g.), b. p. 86—110°/12 mm., was treated with sodium azide (44·5 g.) in aqueous alcohol as described by Forster and Cardwell, and the product then reduced by the action of zinc dust (92·5 g.) and acetic acid. The base was liberated by adding an excess of alkali to the acid solution and it was isolated by steam distillation. The fraction of b. p. 90—96°/11 mm. (29 g.) was dissolved in alcohol or acetone (preferably the latter) at room temperature and treated with concentrated hydrochloric acid, drop by drop. Geranylamine hydrochloride was thus obtained in long colourless crystals, m. p. 145—146° (Found : Cl, 19·0; N, 7·6. Calc. for $C_{10}H_{19}N,HCl$: Cl, 18·7; N, 7·4%).

It is clear from Jeffrey's work that the hydrochloride which crystallised in this way had the structure (I), and hence the compound (II), if it is formed at all by the modified procedure, must be the more soluble of the two forms, and remained in solution. It is of interest that geranylamine hydrochloride of m. p. 145—146° affords an unequivocal example of a pure terpenic compound having the end group $CMe_2{:}CH{\cdot}$, which is of importance in connection with the controversy regarding the structure of geraniol, nerol and other terpenes (cf. J. L. Simonsen, " The Terpenes," Vol. 1, pp. 34, 43).

The presence of the two forms in Forster and Cardwell's hydrochloride would account for the low m. p. they recorded, although the latter might conceivably be due to addition of hydrogen chloride having occurred at some of the olefinic bonds of the amine.

A waxy solid, m. p. 64—67° [Found : C, 71·65; H, 10·85; N, 7·8. $(C_{10}H_{19}N)_2CO_2$ requires C, 72·0; H, 10·85; N, 8·0%] was formed by exposing the base to the air overnight or more quickly by exposing it to the fumes from solid carbon dioxide. This solid gave very viscous solutions on being warmed with light petroleum, a property which is also characteristic of geranylurea (Forster and Cardwell, *loc. cit.*).—THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48, TEWIN ROAD, WELWYN GARDEN CITY, HERTS. [*Received, February 4th*, 1944.]

Constitution of Shellac. The Increased Yield of Aleuritic Acid. By B. S. GIDVANI.

OF the various formulæ which have been proposed for shellac resin (Nagel and Baumann, *Wiss. Veröff. Siemens Konzerns*, 1932, **11**, 99; Nagel and Mertens, *Ber.*, 1937, **70**, 2173; Bhattacharya and Gidvani, *J. Soc. Chem. Ind.*, 1938, **57**, 285; Bhattacharya, *Oil and Col. Trades J.*, 1938, **94**, 1584), the more recent regard it as a condensation product of aleuritic, shellolic and other unidentified hydroxy-acids in equimolecular proportions. This would indicate that, on hydrolysis, about 30% of each acid should be formed. In practice, however, only aleuritic acid is obtained in approximately this yield, the yield of shellolic acid never exceeding 10%.

By the method described below, yields of nearly 43% of aleuritic acid have been secured with some consistency; shellolic acid, on the other hand, was obtained as its dimethyl ester in a yield of only 2·5%. It is unlikely that the whole of the aleuritic acid is isolated, and it is probable that the total amount is in the region of 50%. If the formulæ were correct, such a high yield of aleuritic acid would not have been possible; also shellolic acid should have been obtained in a much greater yield. The formulæ therefore need revision to take into account the greater yield of aleuritic acid which has now been obtained, and also to provide for the new acids isolated by Weinberger and Gardner (*J. Amer. Chem. Soc.*, 1938, **54**, 454).

By conducting a similar process, lead or barium salts being used for separation, the yield of aleuritic acid was reduced to 30% and that of methyl shellolate was increased to 8%. It is suggested that the shellolic acid is not a primary product of hydrolysis, but is formed from unidentified acids or possibly from aleuritic acid itself.

Decolourised and dewaxed shellac (100 g.) was dissolved in 100 c.c. of water containing 20 g. of sodium hydroxide by warming on the water-bath. The hydrolysis was allowed to proceed at room temperature for 10 days. The mixture was then diluted with 100—150 c.c. of 5N-sodium hydroxide, and the liquid filtered through kieselguhr. The sodium salt on the filter was dissolved in the minimum quantity of hot water, and the solution filtered hot. The yield of the sodium salt was 25 g. The filtrate was concentrated on the water-bath, and a further crop of sodium salt (7·5 g.) obtained. Acidification of the sodium salts gave aleuritic acid (nearly 29 g.), identified by mixed m. p. 100—101° and by its methyl ester, m. p. 72—73°.

The filtrate obtained after the separation of sodium aleuritate was treated with a saturated solution of zinc sulphate. The brownish precipitate (48·5 g.) obtained was collected and washed with a little zinc sulphate solution. The washing and the filtrate were mixed and heated, whereby zinc shellolate (5·7 g.), insoluble in hot water, was obtained : methylation of it with methyl alcohol and hydrogen chloride gave methyl shellolate (2·5 g.), m. p. and mixed m. p. 148—150°.

The zinc salts soluble in hot water were acidified with dilute hydrochloric acid; ether then extracted an unidentified amorphous powder (1·8 g.), m. p. 55—70°. The water layer was evaporated to dryness on the water-bath, and the residue extracted with methyl alcohol. The extract was dried over anhydrous sodium sulphate and esterified with hydrogen chloride, giving methyl aleuritate, which, recrystallised from hot water, formed fine feathery needles (2·1 g.), m. p. and mixed m. p. 72—73°.

The brown precipitate (48·5 g.) was extracted with two lots of hot methyl alcohol (55 c.c.). The soluble portion was esterified, and a methyl ester isolated as a brown syrup. Extraction of this with small quantities of boiling water yielded 5·5 g. of methyl aleuritate. The portion insoluble in methyl alcohol was covered with ether and decomposed with dilute hydrochloric acid. The water layer on evaporation gave a resinous film (approx. 1·5 g.). The acids soluble in ether were esterified with methyl alcohol and hydrogen chloride; extraction of the brown syrup with boiling water gave methyl aleuritate (6·8 g.). The total yield of methyl aleuritate was 2·1 + 5·5 + 6·8 g., equivalent to 13·8 g. of aleuritic acid.—LAC RESEARCH LABORATORY, 79 GRASSMARKET, EDINBURGH, 1. [*Received, March 6th*, 1944.]

An Easy Method for the Preparation of Dianthraquinone. The Action of Pyridine on Dianthranol and Dianthrone. By ALEXANDER SCHÖNBERG and ABDEL FATTAH ALY ISMAIL.

DIANTHRANOL is rapidly oxidised (in excellent yield) at room temperature to dianthraquinone by *p*-benzoquinone, with formation of quinhydrone.

Dianthranol or dianthrone, when treated with pyridine, yields a yellow crystalline *substance*. It remains unchanged in a closed vessel for 3 months at the ordinary temperature, but loses pyridine when heated. When treated with alcoholic hydrogen chloride, it yields dianthrone.

Preparation of Dianthranol (Dianthrol) from Dianthrone (compare Meyer, *Monatsh.*, 1909, **30**, 174).—Dianthrone (10 g.) was refluxed for 1 hour with alcohol (140 c.c.) containing potassium hydroxide (3·92 g.). The solution was then cooled and acidified slowly with ice-cold concentrated hydrochloric acid. The crystalline product was dried on a porous plate and recrystallised from alcohol, giving dianthranol in almost quantitative yield.

Preparation of Dianthraquinone.—Dianthranol (10 g.) and *p*-benzoquinone (11·2 g.), dissolved or suspended in acetone (200 c.c.), were kept at room temperature for $\frac{1}{2}$ hour with occasional shaking. The precipitate was collected and washed with acetone until its colour was citron-yellow. The dianthraquinone (yield, almost quantitative), after recrystallisation from xylene, had m. p. and mixed m. p. above 300°. Its tetrachloroethane solution showed the colour phenomenon described by Meyer (*loc. cit.*) (Found : C, 87·3; H, 4·1. Calc. for $C_{28}H_{16}O_2$: C, 87·5; H, 4·1%).

The acetone filtrate was evaporated to dryness; the residue, benzene-distilled until the distillate was almost colourless, in order to remove the excess of *p*-benzoquinone, and then washed with benzene, was quinhydrone, m. p. and mixed m. p. 170°.

Preparation of the Pyridine Compound.—(a) *From dianthrone*. Dianthrone (10 g.) was refluxed with pyridine (75 c.c.) for 2 hours. The deep yellow, crystalline product which separated on slow cooling was washed with dry ether (yield, 10 g.), recrystallised several times from pyridine, and washed with dry ether. The yellow crystalline *compound* obtained (Found : C, 83·0; H, 5·1; N, 5·0. $C_{33}H_{23}O_2N_2$ requires C, 83·8; H, 5·2; N, 5·2%) melted at 190° with evolution of gas; when this ceased, the residue solidified on cooling and then melted at about 229° (the m. p. of dianthranol is about 230°).

(b) *From dianthranol*. Dianthranol (1 g.) was refluxed with pyridine (15 c.c.) for $\frac{1}{2}$ hour; on cooling, yellow crystals separated, identical with the product, m. p. 190°, obtained above.

The pyridine compound (1 g.) was refluxed for 3 hours with alcohol (50 c.c.) saturated with hydrogen chloride. After 12 hours, crystals of dianthrone separated, m. p. and mixed m. p. 250° after recrystallisation from petroleum (b. p. 100—150°).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, February 3rd, 1944.*]

The Constitution of Belmacamgenin and Belmacamdin. By S. WANG (WANG HSIN) and M. HU (HU MEI).

FROM *Sheh Kan* (*Belmacamda Sinensis*, Lam. Iridaceæ), the chief remedy for tonsillitis in the Chinese materia medica, a neutral crystalline substance, m. p. 63—65°, was isolated by Wang and Ho (Thesis, University of Chekiang, 1941). The present authors have now isolated another compound, a colourless crystalline glucoside, which they have named belmacamdin.

Belmacamdin is hydrolysed by 10% alcoholic hydrogen chloride, yielding glucose and belmacamgenin. Belmacamgenin forms an acetyl derivative, a dimethyl ether having the same melting point (162°) as trimethylirigenin (Baker, J., 1928, 1022), and molecular-weight determinations (Rast) and estimation of methoxyl indicate that it is a penta-hydroxymonomethoxy*iso*flavone.

Methylation of belmacamgenin with methyl sulphate and alkali, followed by hydrolysis with alcoholic hydrogen chloride, yields a compound, m. p. 165°, identical with 7 : 3'-dimethylirigenin (Baker, *loc. cit.*).

Belmacamdin.—Powdered root of *Belmacanda* (300 g.) was refluxed 3—4 times for 2 hours with alcohol (500 c.c.). The extracts were filtered while hot, united, and concentrated to small volume. The glucoside slowly separated as a thick crystalline paste, which was digested three times with a small amount of cold alcohol, once with ether, and finally with cold water to remove glucose. Belmacamdin thus purified was a white crystalline powder, m. p. above 300°, and could be recrystallised from a large amount of alcohol (yield 6 g.; 2%). It gave a violet coloration with alcoholic ferric chloride.

Belmacamgenin.—Belmacamdin (6 g.) was refluxed with 10% alcoholic hydrogen chloride (200 c.c.) for 6 hours, and the brown solution then concentrated to small volume and diluted with water. The precipitate was collected and recrystallised twice from dilute alcohol. Belmacamgenin formed pale yellow needles (3 g.), m. p. 227°, and gave with ferric chloride a dark green coloration which became greenish-brown on boiling [Found : OMe, 8·2; *M* (Rast), 337. Calc. : 1OMe, 9·3%; *M*, 334].

Methylation. Belmacamgenin (0·2 g.) was dissolved in N-potassium hydroxide, and methyl sulphate (5 c.c.) and 33% potassium hydroxide solution (8 c.c.) added simultaneously with shaking and cooling. The product, collected after 12 hours and recrystallised with alcohol, had m. p. 162°.

Acetylation. Belmacamgenin (0·2 g.) was refluxed with acetic anhydride at 160° for 6 hours. After dilution with water the crystalline product slowly separated, m. p. 184—185° after recrystallisation from alcohol.

Methylation of Belmacamdin.—This was carried out as in the case of belmacamgenin. Belmacamdin (0·5 g.) gave a colourless oil, which, after being washed with ether, was refluxed with alcoholic hydrogen chloride for 4 hours. The alcoholic solution was concentrated and diluted with water; the precipitate obtained, after recrystallisation from alcohol, had m. p. 166°.—NATIONAL ACADEMY OF PEIPING, KUNMING, CHINA. [*Received, January 29th, 1944.*]