

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

## Food and Drugs

**Colorimetric Determination of the Preservative Value of Hops. Standard Colour Values of Some Hybrid Hops.** A. A. D. Comrie. (*J. Inst. Brewing*, 1940, **46**, 255-256.) —It is pointed out that in the author's colorimetric method for the determination of hop preservative values (*ANALYST*, 1939, **64**, 828) the mixed  $\alpha$ - and  $\beta$ -resins present must be considered in terms of the " $\alpha$ -resin equivalent," *i.e.* the effective sum of the resins when the usually-accepted preservative value of 1/3 of that of the  $\alpha$ -resin is allotted to the  $\beta$ -resin. Thus  $\alpha$  and  $\beta$  per cent. of  $\alpha$ - and  $\beta$ -resin, respectively, in a hop would correspond with an " $\alpha$ -resin equivalent" of  $(\alpha + \beta/3)$  per cent. Similarly, the "standard colour value" (*S.C.V.*) of a hop is, by definition (*loc. cit.*), the colour value of 0.8 mg. of the  $\alpha$ -resin equivalent as it exists in the hop. Since, however, it has been found that the *S.C.V.* for the  $\alpha$ -resin from all sources hitherto examined is a constant, (95) under the conditions of the experiment, whilst the *S.C.V.* for the  $\beta$ -resin depends on the nature of the hop in question, this means that the *S.C.V.* for the mixture will also vary according to the nature of the hop. For

ordinary English varieties, however, this variation has been found to be negligible, and an average value of 82 for the  $\alpha$ -resin equivalent  $(\alpha + \beta/3)$ , could be used. The new hybrid variety "Brewers' Gold" proved an exception (*S.C.V.*, 95), and further determinations have therefore been made on some of the better-known hybrids raised at Wye College. Values found for the *S.C.V.* of the weight of hop containing 0.8 mg. of  $\alpha$ -resin equivalent were, Brewers' Gold, 96; Bullion Hop, 95; Quality Hop, 94; Brewers' Favourite, 91; Early Promise, 93; and Fillpocket, 92. These high figures appear to be due to the high *S.C.V.* of the  $\beta$ -resins (see above), but this in turn does not result from the influence of the species *Humulus americanus* in the inter-specific hybrids, because the wild uncultivated *H. americanus* (var. *neomexicanus*) grown at Wye had an *S.C.V.* of only 82, whilst a further hybrid similar to those above had an *S.C.V.* of 84. It is suggested that if these hybrid hops come into commercial cultivation a *S.C.V.* of 94 should give results in fair accordance with the accepted formula for the gravimetric method,  $10(\alpha + \beta/3)$ ; comparisons of the preservative values obtained by the gravimetric and colorimetric methods confirm this for the above 6 hops. J. G.

\* To be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 3d.

**Fatty Acids and Glycerides of Solid Seed Fats. IX. *Mimusops Heckelii* (Baku) Kernel Fat. D. Atherton and M. L. Meara.** (*J. Soc. Chem. Ind.*, 1940, **59**, 95-96).—*Mimusops Heckelii*, N.O. *Sapotaceae*, is a tree widely distributed in the closed forest areas of the Gold Coast. The nuts, of average weight 20 g., consisted of about 60 per cent. of hard pericarp enclosing 40 per cent. of kernel containing 52 per cent. of fat with the following constants:—saponification equiv. 295.4, iodine value, 52.7; acid value, 2.4; unsaponifiable matter, 0.4 per cent. The component fatty acids in the neutral fat were determined by distillation of the methyl esters; another portion of neutral fat was crystallised from acetone, and the three fractions of increasing solubility were examined. The proportions of fatty acids were computed to be: palmitic, 4.4; stearic, 36.0; arachidic, 0.5; hexadecenoic, 0.3; oleic, 58.5; linolic, 0.3 per cent. by weight. The component glycerides were approximately: steardiolein, 41-47; oleodistearin, 32-26; palmitodiolein, 14-6; triolein, 10-12; oleopalmitostearin, 2-8; fully saturated palmitodistearin 1 mol. per cent. From this analysis and those of other fats, *e.g.* shea butter, it is concluded that when oleic acid approaches 60 per cent. of the mixed fatty acids in a seed fat, triolein is usually present in proportions which, although relatively small, are larger than those of the fully saturated components when the converse relationship holds, *i.e.* the rule of even distribution is less closely followed in the production of the unsaturated glycerides than of the fully saturated glycerides. D. G. H.

**Component Fatty Acids and Glycerides of some *Myristica* Fats. D. Atherton and M. L. Meara.** (*J. Soc. Chem. Ind.*, 1939, **58**, 353-357).—The kernel fats of (a) *Virola surinamensis* from S. America and (b) *Pycnanthus Kombo* (*Myristica angolensis* Walw.) from Sierra Leone were examined. The composition of the nuts was: shell, (a) 17, (b) 14; kernel, (a) 83, (b) 86 per cent., and the kernels yielded to petroleum spirit (a) 71 and (b) 61.6 per cent. of dark brown solid fats. These had saponification equiv. (a) 246.1, (b) 249.9; iodine value, (a) 14.5, (b) 67.0; free fatty acids as oleic acid, (a) 17.2, (b) 18.7; iodine value of neutral fat after removal of highly unsaturated resin acids, (a) 9.9, (b) 32.3. The component acids, estimated by ester fractionation, consisted of (per cent. wt.) decoic, (a) 0.5, (b) 0.2; lauric, (a) 14.8, (b) 11.5; myristic, (a) 72.5, (b) 58.1; palmitic, (a) 4.9, (b) 9.1; tetradecenoic, (a) —, (b) 26.3; oleic, (a) 6.3, (b) 17; unsaponifiable, resins, (a) 1.0, (b) 3.4. Crystallisation from acetone gave fractions the major component glycerides of which were estimated approximately as:—tetradecenodimyrustin, (a) —, (b) 33; trimyrustin, (a) 43, (b) 24; laurodimyrustin, (a) 31, (b) 17; oleolauromyristin, (a) 12; lauromyristopalmitin, (a) 10, and in (b) small amounts of oleotetradecenomyristin, myristoditetradecenoin and laurotetradecenomyristin. The free fatty acids of both fats contained higher pro-

portions of unsaturated acids than those from the neutral glycerides. The kernel fat of *Pycnanthus Kombo* is at present unique in containing 24 per cent. of  $\Delta^9$ -tetradecenoic (myristoleic) acid, an acid not previously reported in seed fats but present in fish and whale oils, and to a small extent in butter-fat. The isomeric dihydroxy acids, m.p. 123° and 81.5° C. respectively, were prepared by mild alkali and acid oxidation of this tetradecenoic acid. D. G. H.

**Fatty Acids and Glycerides of the Seed Fats of *Allanblackia floribunda* and *Allanblackia parviflora*. M. L. Meara and Y. A. H. Zaky.** (*J. Soc. Chem. Ind.*, 1940, **59**, 25-26).—*Allanblackia floribunda* (a) from Nigeria, and *Allanblackia parviflora* (b) from the Gold Coast belong to the N.O. *Guttiferae*. The nuts of *A. parviflora* consisted of 35.5 per cent. of shell and 64.5 per cent. of kernel containing 69.4 per cent. of fat. The analytical constants of the two fats were:—saponification equiv., (a) on refined fat 297.7, (b) 295.3; iodine value (a) on refined fat, 35.4, (b) 37.2; free fatty acids as oleic acid, (b) 1.9 per cent. The fats were examined in the usual way by lead salt separation from alcohol and fractionation of the methyl esters, and the proportions of fatty acids were calculated as:—myristic, (a) —, (b) 1.5; palmitic, (a) 2.9, (b) 2.3; stearic, (a) 57.1, (b) 52.0; arachidic, (a) 0.2, (b) 0.3; oleic, (a) 39.4, (b) 43.9; linolic, (a) 0.4, (b) —. Crystallisation from acetone and examination of the resulting fractions gave data for calculating the glyceride composition to be approximately:—oleodistearin, (a) 76, (b) 60; steardiolein, (a) 15.5, (b) 26-29; oleopalmitostearin, (a) 5.0, (b) 6-9 mol. per cent. Thus the rather small differences in the proportions of fatty acid components in the two fats give rise to greater differences in those of the major components of the glycerides. The fat of *A. parviflora* is seen to be very similar to that of *A. Stuhlmannii* (*J. Soc. Chem. Ind.*, 1931, **50**, 468T; Abst., ANALYST, 1932, **57**, 113). D. G. H.

**Composition of Commercial Palm Oils. V. Partial Separation of Palm Oils by Crystallisation as an Aid to the Determination of the Component Glycerides. T. P. Hilditch and L. Maddison.** (*J. Soc. Chem. Ind.*, 1940, **59**, 67-71).—Two more palm oils have now been examined (*cf. J. Soc. Chem. Ind.*, 1935, **54**, 77T; Abst., ANALYST, 1935, **60**, 328). The two oils: (a) a plantation oil from the Cameroons and (b) a native oil from Grand Bassa, differed in their respective contents of palmitic and oleic acid, and after preliminary separation by acetone into glyceride fractions of relatively simple composition were found to contain the following component fatty acids: myristic, (a) 1.1, (b) 0.6; palmitic, (a) 45.1, (b) 37.6; stearic, (a) 4.1, (b) 3.7; hexadecenoic, (a) 0.8, (b) 1.4; oleic, (a) 38.6, (b) 50.3; linolic, (a) 10.3, (b) 6.4 per cent. by weight. The component glycerides were

approximately (mol. per cent.) "oleo" dipalmitin, (a) 43, (b) 31; palmitodi"olein," (a) 3, (b) 41; "oleo" palmitostearin, (a) 11, (b) 10; tri"olein," (a) 6, (b) 12; tripalmitin, (a) 5, (b) 3; dipalmitostearin, (a) 3, (b) 3; steardi"olein," (a) perhaps up to 1, (b) perhaps traces. Comparison of these figures with those obtained before by progressive hydrogenation (*loc. cit.*) shows that the oils form a series in which the proportion of palmitic acid rises whilst that of oleic acid falls. Summarising, the chief components of palm oils are regarded as "oleo" dipalmitin and palmitodi"olein" in amounts varying according to the proportions of palmitic, oleic and linolic acids in the whole fats. These together usually amount to 70-75 per cent. of the palm oil, "oleo" dipalmitin preponderating in oils of high palmitic acid content and conversely. The minor components are "oleo" palmitostearin (about 10-15) linoleodi"olein" and/or tri"olein" (6-15, varying with the oleic + linoleic acid content of the palm oil), and tripalmitin + dipalmitostearin (3-9 per cent.) varying with the palmitic acid content of the palm oil.

D. G. H.

**Fat of Land Crabs (Seychelles Islands).** T. P. Hilditch and K. S. Murti. (*J. Soc. Chem. Ind.*, 1939, 58, 351-353).—The fat, extracted from land crabs in the Seychelles, consisted of 101.3 g. of a soft yellow solid with saponification equiv. 234.4, iodine value 19.1, free fatty acids, as oleic acid, 1.0, and unsaponifiable matter 0.3 per cent. The fat was systematically crystallised from stated volumes of acetone at 0° C. for 1 day, the mixed fatty acids from each fraction were converted into the methyl esters, and each group was distilled at 0.1 mm. pressure through an electrically heated and packed column. From the data obtained the component acids were computed to be: octoic, 1.5; decoic, 5.3; lauric, 47.5; myristic, 14.0; palmitic, 13.1; stearic, 1.7; tetradecenoic, 0.7; hexadecenoic, 2.2; oleic, 5.3; linolic, 1.5; unsaturated  $C_{20-22}$  acids, 2.2 mol. per cent. The fat contained 66.3 per cent. of fully saturated glycerides of which the component acids included octoic, 3.2; decoic, 7.1; lauric, 54.8; myristic, 20.5; palmitic, 12.7; stearic, 1.7 mol. per cent. The striking resemblance between the fatty acids and those of seed fats of the palm family, and the almost entire absence of the characteristics of a typical marine animal fat are probably accounted for by the fact that these crabs feed on coconuts.

D. G. H.

**Alkaloids of some *Chondrodendron* Species and the Origin of *Radix Pareirae Bravae*.** H. King. (*J. Chem. Soc.*, 1940, 737-746).—Differences in the optical rotatory power of bebeerine from different samples of the drug *Radix Pareirae Bravae* are attributed to its origin in two very similar species, *Chondrodendron platyphyllum* and *Ch. microphyllum*. These yield *l*- and *d*-bebeerine, respectively, the latter occurring in the drug on the English market. From these species,

from *Ch. candicans* (the British Guiana species) and from the drug, alkaloids were obtained as follows:—*Ch. platyphyllum* (Rio) root (924 g.):—*d*-iso-chondrodendrine (sulphate 43.1 g. plus base 1.7 g.), *l*-bebeerine (9.0 g.), *Ch. platyphyllum* (Bahia), root: (720 g.), *l*-bebeerine (hydrochloride 55.3 g. plus base 1.50 g.), *d*-iso-chondrodendrine (hydrochloride 1.1 g. plus base 0.65 g.); stems (538 g.): *l*-bebeerine (28.32 g.); leaves (300 g.): *l*-chondrofoline, *d*-isochondrodendrine, *l*-bebeerine (total crude alkaloid 3.4 g.) *Ch. microphyllum* (Bahia), root (845 g.): *d*-isochondrodendrine (sulphate 18.3 g. plus base 1.42 g.), *d*-bebeerine (hydrochloride 15.4 g. plus base 1.5 g.). *Ch. candicans* (British Guiana), stems (1500 g.): *d*-isochondrodendrine (hydrated sulphate 17.7 g. plus base 1.48 g.), *d*-bebeerine (4.93 g.). *Pareirae Bravae*: *d*-bebeerine *d*-isochondrodendrine, *d*-isococlaurine. The widely differing proportions of alkaloids in the same species are ascribed to climatic and seasonal causes. The new alkaloids *l*-chondrofoline and *d*-isococlaurine are related to bebeerine and isomeric with coclaurine respectively. Chondrofoline,  $C_{33}H_{36}O_6N_2$ , is phenolic and contains three methoxyl groups; methylation yields an amorphous *O*-methyl methiodide and methochloride closely resembling the corresponding products from bebeerine, while other reactions give products identical or enantiomorphous with those from bebeerine. The alkaloid does not give the Millon reaction and contains only one phenolic group. Isococlaurine, which was isolated from a relatively large amount of *Radix Pareirae Bravae*, is phenolic and contains one methoxyl group. The derivative on complete methylation, *d*-*O*-dimethyl-*N*-methylcoclaurine methiodide, is the optical enantiomorph of the similar product from natural *l*-coclaurine. The alkaloid gives the Millon reaction and does not give the catechol reaction. Probable structural formulae for the two alkaloids are given. The study of *d*-isochondrodendrine has enabled probable structures to be assigned to proto-curidine and neoprotocuridine, isomeric phenolic alkaloids of pot-curare; many bisbenzylisoquinoline alkaloids can also be classified as either bebeerine or isochondrine types.

E. B. D.

**Separation and Determination of Isomeric Menthols.** R. T. Hall, J. H. Holcomb, Jr., and D. B. Griffin. (*Ind. Eng. Chem., Anal. Ed.*, 1940, 12, 187-188).—The synthetic menthol used to replace Menthol U.S.P. (*l*-menthol from *Mentha arvensis*) consists of varying mixtures of the other isomers with some of the U.S.P. product, the number and proportion of isomers depending upon the method of synthesis. When *d*-citronellal (from citronella oil) is the initial material a mixture of 3 isomers, *viz.* *d*-neomenthol, *d*-isomenthol and *l*-menthol, is obtained and the large proportion of *l*-menthol in this particular mixture makes its commercial separation possible. The analytical reactions of these isomers have been studied. Most methods for the determination of total menthol depend

upon acetylation followed by hydrolysis of the acetylated product with alcoholic potassium hydroxide solution. Saponification with a solution of potassium hydroxide in diethylene glycol (Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 521; Abst., *ANALYST*, 1938, **63**, 62) reduces the time of hydrolysis to one-fourth or one-fifth. The rates of both the acetylation and the hydrolysis vary for the different isomers. Acetylation for 2 hours is sufficient, and low results obtained for some of the isomers were invariably due to incomplete hydrolysis. Hydrolysis of the esters of *l*-menthol and *d*-isomenthol with 0.5 *N* alcoholic potassium hydroxide was practically complete within 30 minutes, but the *d*-neomenthol ester required 3.5 hours. The more rapid hydrolysis effected by the diethylene glycol solution of potassium hydroxide did not affect the accuracy of the results; again, however, the *d*-neomenthol ester (and consequently the isomeric mixture) required a longer time for hydrolysis than the esters of the other isomers.

A. O. J.