246. *Sapogenins. Part V. Bassic Acid.*

By B. Jason Heywood, George A. R. Kon, and Lancelot L. Ware.

A new sapogenin, *bassic acid*, $C_{30}H_{46}O_5$, has been isolated from several species of *Bassia* and shown to be an acid of the triterpene series. It has two hydroxyl groups in the 1 : 3-position to one another, like those of hederagenin and occupying the same position in the molecule; the carboxyl group and a double bond also occupy positions similar to those of other sapogenins. There is another hydroxyl and a reactive double bond, the positions of which still remain to be determined. A partial formula for the compound is suggested.

The poisonous properties of Mowrah meal, the residue remaining after the oil has been pressed from the seeds of the Indian butter tree, *Bassia Latifolia* Roxb., have long been utilised for the destruction of earth worms on lawns and golf courses, but little is known of the poisonous constituent itself.

Moore, Sowton, Baker-Young, and Webster (*Biochem. J.*, 1910, **5**, 94) showed that the meal contained 2% of a bitter glucoside, mowrin, with a digitalis-like action on the heart of the frog; this was readily hydrolysed to an aglucone, mowric acid, which was, however, amorphous and could not have been a pure sapogenin, judged from its high oxygen content. Spiegel (*Ber. deut. pharm. Ges.*, 1918, **28**, 100) extracted 10% of glucoside from the meal of *B. Latifolia* and obtained two aglucones, crystalline mowragenic acid, $C_{19}H_{30}O_6$, and amorphous mowrageninic acid, $C_{19}H_{28}O_5$; he suggested that the previous authors were dealing with the meal of *B. Latifolia*, which is the tree commonly grown in Central India, and not *B. Longifolia* L. as stated in their paper.

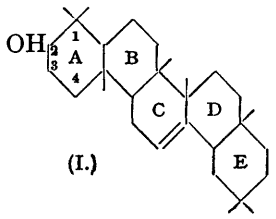
As supplies of raw material are abundant, it seemed of interest to reinvestigate the mowrah sapogenins, the properties of which suggested that they might be related to the acids of the triterpene series. We have used commercial mowrah meal, also seeds of *B. Latifolia* from the Central Provinces, and those of *B. Butyracea* L., the last kindly obtained for us by Dr. N. L. Bor of the Forest Research Institute, Dehra Dun, from the Lohaghat Range, East Almora Division, U.P. In all cases extraction of the fat-free meal with alcohol and precipitation with ether gave the crude saponin in about 20% yield. The material obtained from commercial mowrah meal was dark and intractable, but from *B. Butyracea* seeds we obtained up to 27% of a colourless crystalline product which was no longer deliquescent like the cruder preparations (contrast Moore *et al.*, *loc. cit.*). The composition of it corresponds roughly to $(C_2H_4O)_x$. The saponin is extremely readily hydrolysed by mineral acids, the solution setting to a jelly, as already observed by previous investigators, but it is possible under certain conditions to obtain a product isolable by filtration, and if this is washed free from water-soluble impurities and dried, it can be purified without much difficulty. For the preparation of the sapogenin it is not necessary to isolate the saponin and a water extract of the meal can be used. The pure sapogenin is very sparingly soluble and crystalline, with the high m. p. of 316°, and is clearly different from the products described by previous workers in this field; the name *bassic acid* is suggested for it.

The same sapogenin has also been obtained, although in somewhat poorer yield, from the press-cake of the shea nut, *Bassia* (*Butyrospermum*) *Parkii* Ktschk., from W. Africa. This finding shows that bassic acid must be widely distributed in the seeds of *Bassia* spp. and related plants; it has an additional interest, because the shea nut has already been shown to contain the triterpene alcohol basseol (Heilbron, Moffet, and Spring, J., 1934, 1583) as well as lupeol and α-amyrin.

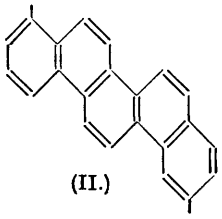
Bassic acid crystallised from ethyl acetate has the formula $C_{30}H_{46}O_5,H_2O$, and from methyl alcohol a product containing a molecule of the latter solvent is obtained; a similar alcoholate is formed with butyl alcohol, but an anhydrous preparation has been obtained by prolonged drying of a sample crystallised from dioxan. The acid is monobasic on titration and gives a crystalline *methyl* ester, $C_{31}H_{48}O_5$. The melting points of the acid and its ester and their optical rotations are remarkably close to the constants found by van der Haar (*Rec. Trav. chim.*, 1929, **48**, 1155, 1166) for a sapogenin isolated from both

Achras Sapota L. and *Mimusops Elengi* L.; his compound, however, is described as being anhydrous after crystallisation from alcohol. It is hoped to institute a comparison of this sapogenin with bassic acid.

The dehydrogenation of bassic acid with selenium has only been carried out on a small scale, but the results show that it behaves like a typical triterpene; the principal product isolated was sapotalene (1 : 2 : 7-trimethylnaphthalene), accompanied by 2 : 7-dimethylnaphthalene and a small amount of 1 : 8-dimethylpicene.* The phenolic fraction was obtained in such small amount that it could not be completely purified, but there is little doubt that it consisted of hydroxyagathalene (6-hydroxy-1 : 2 : 5-trimethylnaphthalene). The isolation of 1 : 8-dimethylpicene (II) shows that bassic acid has the same carbon skeleton (I) as other typical sapogenins, such as hederagenin. The production of hydroxyagathalene (III), if confirmed, would prove that one hydroxyl group of bassic acid occupies the characteristic position on C_2 as in other triterpenes.



(I.)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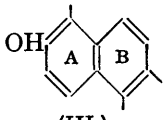
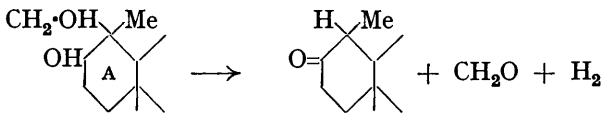


(III.)

The further elucidation of the structure of bassic acid has proved extremely difficult, because only a very few of its derivatives can be obtained crystalline; we have so far been unable to obtain a satisfactory benzoate, acetate or tribromoacetate and the nature of the oxygen atoms can only be inferred from determinations of active hydrogen (Zerevitinov). These suggest that all three oxygen atoms are contained in hydroxyl groups and this is supported by the preparation of a *triacetyl* ester, which has been obtained crystalline by sublimation in a high vacuum, although it could not be made to crystallise from any of the solvents tried.

A further inference is possible from the preparation of a crystalline *acetonyl* derivative from the methyl ester, similar to that prepared from hederagenin methyl ester by Jacobs (*J. Biol. Chem.*, 1925, **63**, 631). This is the most characteristic derivative so far obtained from bassic acid; its composition has been checked by numerous analyses and it has been shown to retain one active hydrogen atom. The two hydroxyl groups involved in its formation must be in the 1 : 3-position to each other, like those of hederagenin. Moreover, it can be shown that one of these is a primary one, because the ester undergoes oxidation by means of copper bronze in exactly the same manner as hederagenin methyl ester (Tsuda and Kitagawa, *Ber.*, 1938, **71**, 1604); one atom of carbon is eliminated as formaldehyde and the product is a neutral diketone, $C_{30}H_{44}O_4$, isolated in the form of its 2 : 4-*dinitrophenylhydrazone*. This decomposition is formulated as follows:

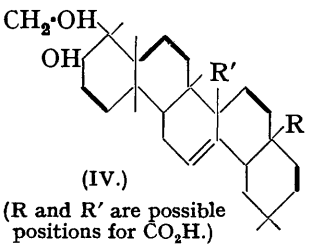


Bassic acid is unsaturated to tetranitromethane. The formula $C_{30}H_{46}O_5$ has two hydrogen atoms less than the number required for a pentacyclic trihydroxy-acid with one double bond and the acid differs from the majority of triterpene acids in having two double bonds. One of these is comparatively reactive and bassic ester is hydrogenated to *dihydrobassic* ester; the acid is only hydrogenated with some difficulty to an amorphous dihydro-acid. The ester readily forms a somewhat unstable *dibromide*. All these compounds are still unsaturated to tetranitromethane, showing the presence of an additional

* We are particularly indebted to Prof. L. Ruzicka for comparing our specimen with his synthetic 1 : 8-dimethylpicene and establishing their identity.

double bond which is inert, like that encountered in other sapogenins. This inert double bond occupies a $\beta\gamma$- or $\gamma\delta$-position with respect to the carboxyl group, because both bassic acid and dihydrobassic acid are readily lactonised when treated with hydrogen bromide in acetic acid; the lactones formed are, unfortunately, amorphous. A crystalline *bromolactone* is, however, formed when bassic acid is treated with bromine in acetic acid.

The absorption spectrum of bassic ester shows no absorption bands attributable to conjugated double bonds and it follows also that the double bonds are not in the $\alpha\beta$-position with respect to the carboxyl. It can be assumed that the inert double bond occupies a position similar to that in hederagenin; the carboxyl group must occupy a "protected" position, because the ester is hydrolysed with difficulty. The triterpene skeleton first put forward by R. D. Haworth (*Ann. Reports*, 1937, 327 *et seq.*) being adopted, the structure of bassic acid can be represented by (IV). The thick lines represent possible positions for the active double bond, and another hydroxyl, presumably a secondary one, remains to be accommodated. The number of possibilities is limited by the fact that the dinitrophenylhydrazone mentioned on p. 1125 evidently contains the group :C·C:N·NHR, because its absorption spectrum shows maxima at 3900 and 2600 A. with an inflection at 2930 A. (log ε 4·42, 4·17, and 3·99 respectively). The carbonyl group which has reacted with dinitrophenylhydrazine must therefore be part of a conjugated system formed either by another carbonyl group on the adjoining carbon atom or by a doubly bound carbon atom. The further discussion of this point is reserved until fresh experimental material becomes available.



(IV.)
(R and R' are possible positions for CO_2H.)

Experimental.

Extraction of the Saponin.—(i) *From* B. Butyracea. The seed kernels (75% by weight of the seeds) were minced, and the meal (156 g.) extracted (Soxhlet) with light petroleum (b. p. 40—60°) for 12 hours, 90 g. of solid, pale yellow fat being thus removed. The fat-free meal (66 g.) was then extracted for 36 hours with absolute (or, better, 95%) alcohol. The colourless extract was poured into ether (3 vols.) and the crude saponin (18 g. or 27% of the fat-free meal) filtered off and dried over phosphoric oxide in a vacuum. The saponin could be recrystallised by dissolving it in the minimum amount of hot alcohol and adding ether (3 vols.); it separated in feathery needles, m. p. 235—240° (decomp.) (Found: C, 55·8; H, 9·4%). When pure, the saponin was not deliquescent. It had no reducing properties; an alcoholic solution formed a precipitate with cholesterol, but the precipitation was far from complete.

On a large scale the fat-free meal was extracted by boiling three times with 95% alcohol, which was then poured into ether (3 vols.). The crude saponin was filtered off, washed twice with ether without being allowed to dry on the filter, and immediately hydrolysed to the sapogenin.

(ii) *From* B. Latifolia. The seeds of *B. Latifolia*, obtained by Messrs. A. Boake Roberts and Co. of Stratford from different localities in the Central Provinces of India, gave in addition to 47% of fat a somewhat lower yield of saponin (17% calc. on the fat-free meal) and this was always coloured. A similar material was also obtained from commercial mowrah meal. A quantity of crude saponin was prepared for us by Messrs. A. Boake Roberts by extraction of the meal with water and evaporation.

(ii) *From the shea nut*, B. Parkii. The dark brown, coarsely ground press-cake from the extraction of shea nut fat, obtained from the British Extracting Co., Wilmington, Hull, was extracted with petroleum to remove some 2% of residual fat and yielded 15% of dark brown saponin containing some crystals.

Bassic Acid.—The saponin from *B. Butyracea* (1700 g.) was dissolved in 10 l. of 5% hydrochloric acid, and the solution boiled for 6 hours. The sapogenin, which at first separated in a jelly-like form, became granular and could be filtered off; it was purified by two or more extractions with hot water to remove sugars, etc., and dried in a vacuum desiccator. The crude sapogenin was then extracted with pure dry ethyl acetate for 3 days in a modified Soxhlet apparatus in which the solvent percolated continuously through the material to be extracted and did not accumulate. The light brown solid obtained by removal of the solvent could be decolourised by boiling a methyl-alcoholic solution with norit and crystallised from the con-

centrated solution (alternatively, the extraction with ethyl acetate can be repeated). The yield of pure sapogenin was 19 g.

The same method was used for the preparation of the sapogenin from *B. Latifolia* seeds and from commercial mowrah meal, but the material was more difficult to purify and required repeated extractions with hot water. The sapogenin can also be prepared direct from the meal, without isolation of the saponin; the fat-free meal is extracted with hot water, hydrochloric acid added to give a 5% solution, and the solution boiled. The yield is not as good as when the saponin is isolated.

The sapogenin from *B. Parkii* was obtained as a gum after this treatment, although a little crystalline material separated from the ethyl acetate solution after the bulk of the gum had been filtered off. A pure crystallisable solid was, however, obtained by extracting the gum with 10% potassium hydroxide solution, which left some material undissolved, and reprecipitation with mineral acid; the precipitated solid was recrystallised from methyl alcohol (norit).

The sapogenins from all these sources proved to be identical:

	From *B. Butyracea.*	From *B. Latifolia.*	From *B. Parkii.*
M. p.	316°	316°	308—309°
$[\alpha]_D$	+ 82·4° (*c* = 1·86 in pyridine)	+ 82·4° (*c* = 1·42 in pyridine)	+ 82·9° (*c* = 1·90 in pyridine)
Ester, m. p.	209°	210—212°	211—212°
$[\alpha]_D$	+ 64·0° (*c* = 2·01 in chloroform)	+ 63·0° (*c* = 2·21 in chloroform)	+ 63·6° (*c* = 1·60 in chloroform)

Bassic acid crystallised from ethyl acetate retains a molecule of water of crystallisation (Found: C, 71·2, 71·7; H, 9·6, 9·4. $C_{30}H_{46}O_5,H_2O$ requires C, 71·4; H, 9·6%) and this is supported by the results of titration in alcoholic solution (Found: *M*, 501·3, 503·0, 504·0, 503·9, 506·4. Calc., 504·7). After crystallisation from methyl alcohol the acid retains a molecule of the solvent even after drying for 2 hours at 110°/2 mm. (Found for a specimen from *B. Latifolia*: C, 72·2, 72·2, 72·3, 72·1; H, 9·4, 9·5, 9·3, 9·3; for a specimen from *B. Parkii*: C, 72·7; H, 9·5. $C_{30}H_{46}O_5,CH_4O$ requires C, 71·8; H, 9·7%). If *n*-butyl alcohol is used for the purification of the sapogenin after preliminary treatment with ethyl acetate, a similar alcoholate, m. p. 319°, is obtained (Found: C, 73·0, 72·9; H, 9·7, 9·7. $C_{30}H_{46}O_5,C_4H_{10}O$ requires C, 72·8; H, 10·0%). The slightly high values for carbon are no doubt due to some loss of solvent on drying. A solvent-free specimen of the acid was obtained by crystallising the acid, purified by ethyl acetate, from dioxan–petroleum. After drying for 3 hours at 110°/0·0004 mm., it still retained some solvent (Found: C, 72·8; H, 9·5%), but after 25 hours' drying it was solvent-free (Found: C, 73·8; H, 9·5. $C_{30}H_{46}O_5$ requires C, 74·1; H, 9·5%); at the same time the m. p. fell from 316—317° to 303°.

Methyl Ester.—This is best prepared with the aid of diazomethane (75% yield); a 50% yield of a less pure ester can be obtained with methyl sulphate and alkali. The ester prepared by heating the tetramethylammonium salt of the acid (Prelog and Piantanida, *Z. physiol. Chem.*, 1936, **240**, 36) did not crystallise, but could be converted into the crystalline acetonyl derivative (see below) identical with that prepared in the usual way. The ester crystallised from dilute alcohol separated as a hydrate (?), m. p. 183—184°, but from acetone or benzene–petroleum fine prisms, m. p. 212°, were obtained (Found: C, 74·3, 74·4; H, 9·8, 9·7; for a specimen from *B. Parkii*: C, 74·1; H, 9·4. $C_{31}H_{48}O_5$ requires C, 74·4; H, 9·7%). The purity of the ester was checked by chromatographing a benzene solution of it and dividing it into a number of fractions; apart from a minute amount of gummy impurity adsorbed at the top of the column, all the fractions gave an ester with the same m. p.

Titration with permonophthalic acid indicated 1·07 and 1·09 double bonds, cholesterol being used as a standard of comparison. The ester was unchanged after boiling for 3 hours with an excess of 5% methyl-alcoholic potassium hydroxide; about 60% hydrolysis occurred after boiling for 24 hours with 4N-ethyl-alcoholic potassium hydroxide.

Dibromobassic Ester.—0·5 G. of the methyl ester in 50 c.c. of chloroform was treated with 10 c.c. of 3·5% bromine in chloroform. The solution rapidly deposited the *dibromide* (0·26 g.), which was very sparingly soluble in chloroform and was purified by washing with this solvent; it formed small needles, m. p. 133—135°. The crude compound was analysed after drying in a vacuum at room temperature (Found: C, 56·0; H, 7·6. $C_{31}H_{48}O_5Br_2$ requires C 56·4; H, 7·3%); it decomposed on recrystallisation.

Methyl Dihydrobassate.—The methyl ester (0·48 g.) in 25 c.c. of acetic acid was shaken with 0·6 g. of Adams's catalyst in hydrogen for 14 hours. After removal of the catalyst and addition

of water the *ester* was filtered off and crystallised successively from alcohol, acetone, and benzene–petroleum; it formed stout, transparent prisms, m. p. 172—173°, not depressed by admixture of methyl bassate, and gave a yellow colour with tetranitromethane in chloroform solution (Found: C, 74·3; H, 10·0. $C_{31}H_{50}O_5$ requires C, 74·1; H, 10·0%).

Dihydrobassic Acid.—The acid was hydrogenated in the same way as the ester; after precipitation with water an amorphous solid was obtained, which has not yet yielded a crystalline product.

Acetonyl Derivative of the Methyl Ester.—The ester (0·5 g.) was dissolved in the minimum amount of dry acetone and treated with 3 drops of concentrated hydrochloric acid. Prisms of the new *compound* soon began to separate and were collected after several hours; m. p. 205° (Found: C, 75·4, 75·5, 75·2, 75·4; H, 9·5, 9·8, 9·6, 9·8; for a specimen from *B. Parkii*: C, 75·3; H, 9·4. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%). Several crystallisations from acetone sufficed to reconvert the compound into the methyl ester (Found: C, 74·2, 74·1; H, 9·3, 9·4. Calc.: C, 74·4; H, 9·7%).

Triacetylbassic Acid.—3 G. of bassic acid were boiled for an hour with 30 c.c. of acetic anhydride, the excess of reagent destroyed by means of methyl alcohol, and the mixture poured into water with rapid stirring. The white precipitate obtained could not be crystallised from any of the solvents tried; it was partly purified by solution in alcohol and reprecipitation with water. Evaporation of a methyl-alcoholic solution at room temperature in a vacuum gave a yellow powder of crystalline appearance, m. p. 117°; for analysis, this crude material was dried over silica gel in a vacuum desiccator (Found: C, 67·9, 67·6; H, 8·4, 8·4; CH_3·CO, 23·0. $C_{36}H_{54}O_8,H_2O$ requires C, 68·3; H, 8·9; CH_3·CO, 20·4%). The *methyl* ester was prepared with the aid of diazomethane and proved too soluble in all the usual solvents to be recrystallised; it was twice sublimed at 150°/0·01 mm., and formed a crystalline solid, m. p. 95—96° (Found: C, 70·9, 71·1; H, 8·9, 8·9. $C_{37}H_{54}O_8$ requires C, 70·9; H, 8·7%). On alkaline hydrolysis it yielded methyl bassate in a pure condition.

Acetyl-lactone.—A solution of 5 g. of bassic acid in 50 c.c. of acetic acid was kept cooled in ice and saturated with dry hydrogen chloride. The solution was then boiled under reflux for 6 hours, cooled, resaturated with hydrogen chloride, again boiled, and finally poured into water. The precipitate was dissolved in chloroform–ether, and the solution washed with 20% alkali, which removed a good deal of triacetyl acid. The neutral product, isolated in poor yield, formed a yellow powder which could not be purified. A better yield of equally intractable material was obtained when zinc chloride was added to the reaction mixture and a similar product resulted on carrying out the reaction without heating.

Bromo-lactone.—A solution of 1 g. of bassic acid and 4 g. of sodium acetate in 90 c.c. of acetic acid and 10 c.c. of water was treated dropwise with 30 c.c. of 3% bromine in acetic acid. After 2 hours the solution was poured into water containing a little sodium hyposulphite. The crystalline precipitate was washed with 10% potassium carbonate solution, then water, and recrystallised three times from dilute acetic acid, forming small needles, m. p. 220° (Found: C, 63·7; H, 8·4. $C_{30}H_{45}O_5Br$ requires C, 63·7; H, 8·0%).

Oxidation of the Methyl Ester.—3·7 G. of the methyl ester were ground with 7·4 g. of fat-free copper bronze and heated in a mixed nitrate bath at 285° for ¾ hour; the issuing gases were passed through a solution of dimethyldihydroresorcinol and produced a flocculent precipitate due to formaldehyde. The reaction product was distilled at 140—165°/0·0008 mm., forming a brown glassy solid. This was dissolved in benzene, percolated through a column of activated alumina (20 g.), and recovered by evaporation. The solid was dissolved in 80 c.c. of alcohol and 8 c.c. of acetic acid and boiled for an hour with 1·1 g. of Girard's reagent " T ", the cooled solution poured into 150 c.c. of ice-water containing 6 g. of sodium hydroxide, and the solution diluted to 450 c.c. and extracted three times with ether. The aqueous layer was treated with dilute sulphuric acid until the concentration of acid was 0·75N, kept for an hour, and re-extracted with ether; 0·5 g. of a yellow gum was recovered after removal of the solvent. This was boiled in alcoholic solution with 0·8 g. of 2 : 4-dinitrophenylhydrazine, dissolved in hydrochloric acid, for ¾ hour, and the solid collected when cold. It was purified by solution in benzene–petroleum (b. p. 60—80°) (1 : 4) and percolation through a 35-g. column of activated alumina. The 2 : 4-*dinitrophenylhydrazone* was strongly adsorbed and formed a distinct band apart from a small band at the top of the column which contained tarry material. It was recovered by elution with hot alcohol and further purified from this solvent, separating as an apparently amorphous, brick-red solid, m. p. 184° with previous softening (Found: C, 66·9; H, 7·6; N, 9·2. $C_{36}H_{46}O_7N_4$ requires C, 66·9; H, 7·2; N, 8·8%).

Dehydrogenation of Bassic Acid.—35 G. of bassic acid and 70 g. of selenium were heated for

24 hours at 290—300° and for a further 48 hours at 320—330° (temperature of mixed nitrate bath). The products were then exhaustively extracted (Soxhlet) with ether (extract A) and with benzene (extract B).

Extract A was filtered and shaken with 10% alkali solution in an atmosphere of nitrogen, the alkaline extract being at once poured into dilute acid (fraction C). The ethereal solution was distilled (long column), leaving 10 g. of residue, which was extracted in portions with 300 c.c. of petroleum (b. p. 60—80°), leaving a solid D; a little more solid, E, was deposited from the petroleum solution on cooling. The clear solution was then run through a small column of activated alumina and evaporated, yielding a golden oil, which was distilled. The following fractions were collected: (i) up to 134°/9 mm., 0·6 g. of pale yellow oil depositing solid 2 : 7-dimethylnaphthalene; (ii) 134—144°/9 mm., 0·45 of pale yellow oil; (iii) 150—170°/9 mm., 0·45 g. of yellow oil; (iv) at 2 mm. with free flame, 0·6 g. of deep yellow oil; (v) at 2 mm. with free flame, 0·5 g. of red oil; leaving (vi) 0·6 g. of a tarry mass.

Fraction (i) was treated with *s*-trinitrobenzene, and the product fractionally crystallised from alcohol; the least soluble fraction (ia) melted at 138° and was added to the corresponding fraction from (ii). The more soluble fraction could not be satisfactorily resolved into its components and was therefore reconverted into the hydrocarbons, and these treated with picric acid. The less soluble portion of the picrates was repeatedly crystallised from alcoholic picric acid and gave needles, m. p. 142°, which were identified as 2 : 7-dimethylnaphthalene picrate by direct comparison (mixed m. p.) with a synthetic specimen; unfortunately, the specimen decomposed before it could be analysed, but a small amount of hydrocarbon, m. p. and mixed m. p. 96°, was obtained from it.

From the mother-liquors of 2 : 7-dimethylnaphthalene picrate a minute amount of a red picrate, m. p. 96°, was isolated, presumably the picrate of 1 : 2 : 3 : 4-tetramethylbenzene.

Fraction (ii) gave a pale orange *s*-trinitrobenzene derivative, m. p. 137°, which was combined with (ia) and repeatedly crystallised from alcohol until the constant m. p. 147° was reached, not depressed by admixture with the corresponding derivative of sapotalene (Found: C, 59·9; H, 4·4. Calc.: C, 59·6; H, 4·5%). The liquid hydrocarbon was regenerated from this and converted into the picrate and the styphnate, which were found to be identical with the appropriate derivatives of sapotalene.

The remaining fractions gave deep red trinitrobenzene derivatives, but these could not be satisfactorily separated into their constituents.

The buff solid D (0·84 g.) could not be recrystallised and did not form a crystalline compound with 2 : 7-dinitroanthraquinone. It was therefore sublimed at 210°/0·01 mm., a yellow powder being obtained in poor yield. This was crystallised from xylene, then from *iso*butyl acetate (norit); after two more crystallisations from the latter solvent it formed colourless plates which looked grey in reflected light, m. p. 298°. Prof. L. Ruzicka found the m. p. to be 307—308° (corr., in sealed capillary), not depressed by admixture with synthetic 1 : 8-dimethylpicene (Found: C, 93·7; H, 6·3. Calc. for $C_{25}H_{20}$: C, 93·7; H, 6·3%. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). The analytical figures are in better agreement with those required for a trimethyl- rather than a dimethyl-picene. A further small amount of the same hydrocarbon was isolated from the solid E and the benzene extract B.

The phenolic fraction C was only obtained in very small amount and was converted into the methyl ether, which formed a grey solid. It was converted into the *s*-trinitrobenzene complex, the m. p. of which reached 138° when further crystallisation became impossible; the methoxy-compound regenerated from it by passing a benzene solution through a column of activated alumina had m. p. 86—87°. These properties suggest that the substance was almost certainly slightly impure methoxyagathalene (6-methoxy-1 : 2 : 5-trimethylnaphthalene), which melts at 89—90°, and its *s*-trinitrobenzene compound at 146—147° (Ruzicka, Hofmann, and Schellenberg, *Helv. Chim. Acta*, 1936, **19**, 1391).

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