X.—*Campnospermonol, a Ketonic Phenol from* Campnospermum brevipetiolatum.

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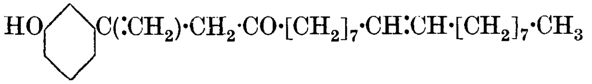
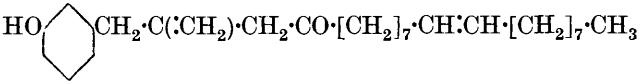
Campnospermum brevipetiolatum (N.O. *Anacardiaceæ*), a large tree endemic in the Sepik River district, Mandated Territory of New Guinea, is stated by C. E. Lane Poole ("Forest Resources of the Territories of Papua and New Guinea," p. 106) to yield on tapping an oily exudate used by the natives as a substitute for cocoanut oil.

This material, received through the instrumentality of Mr. Lane Poole, consists principally of a ketonic phenol, $C_{27}H_{42}O_2$ or $C_{28}H_{44}O_2$, of phytochemical interest because of the association of the oleyl radical with an aromatic residue and possible generic connexion with the fatty oils, and represented by one of the constitutional formulæ



β-*m*-hydroxyphenyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one

and



β-*m*-hydroxybenzyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,

the results of investigation failing to distinguish between these. The ketonic phenol, which we propose to designate *campnospermonol*, is conveniently isolated in the form of the more stable *methyl* ether by distillation of the latter under reduced pressure.

It is characterised chemically by solubility in caustic alkali, reactivity with acetic anhydride, and capacity for oxime formation. The iodine values and the ready addition of four atoms of hydrogen under the influence of platinum as catalyst afford evidence of the existence in campnospermonol and campnospermonyl methyl ether of two ethenoid linkages. That neither linkage is conjugated with respect to the carbonyl group follows from the non-occurrence of the usual reactions of αβ-unsaturated ketones and from the normality of the molecular refraction.

Ready oxidation of campnospermonyl methyl ether in cold acetone solution by means of potassium permanganate produces *m*-methoxybenzoic, azelaic, formic, and nonoic acids, the last-named in quantitative yield. No dibasic acid other than azelaic was detected. Definite evidence of the attachment of a methylene group in the chain is the production of formic acid by oxidation with ozone of the methyl ether in chloroform, there being obtained also nonoic acid and nonoaldehyde, together with long-chain acid and aldehydic substances the constitutions of which were not experimentally ascertained.

Reduction of campnospermonyl methyl ether by hydrogen in presence of platinum produced *hydrocampnospermonyl methyl ether*, $C_{28}H_{48}O_2$ or $C_{29}H_{50}O_2$, a crystalline ketone, yielding a crystalline *oxime* and producing on oxidation in acetone by potassium permanganate *m*-methoxybenzoic, margaric, and oxalic acids.

The acid product of the action of phosphorus pentachloride on the oximino-derivative of hydrocampnospermonyl methyl ether consisted largely of stearic acid with a smaller amount of undetermined, presumably aromatic, acid. Accidental loss of the bulk of the nitrile simultaneously produced in this reaction precluded other than its cursory examination. The mixture of acids obtained on hydrolysis of the nitrile was mainly aromatic, but contained a small amount of fatty acid, probably margaric. The results, while indicating that the oximino-derivative probably consisted of two isomerides, one in preponderating amount, serve, from the fact of the direct production of stearic acid, to fix the position of the carbonyl group definitely as indicated in the chain.

Conclusive evidence has not been obtained as to the exact constitution of that portion of the chain comprising the attached methylene group and situated between the carbonyl group and the aromatic nucleus, although the acetyl value (128) determined for crystalline *hydrocampnospermonyl acetate* appears to favour the first of the formulæ proposed.

Reduction of the carbonyl group of campnospermonyl methyl ether to methylene by Clemmensen's method (*Ber.*, 1913, **46**, 1837) and subsequent hydrogenation of the ethenoid linkages yielded the saturated methoxy-hydrocarbon, β-*m*-methoxyphenylheneicosane or β-*m*-methoxybenzylheneicosane.

Further work on campnospermonol and its derivatives is contingent on the receipt of additional material. In view of the remoteness of the source of supply, however, postponement of publication of the results already obtained is deemed inadvisable.

EXPERIMENTAL.

The exudate, a dark, somewhat viscous liquid having the superficial characteristics of a fatty oil, an odour reminiscent of the higher fatty acids, and the constants $d^{15\cdot5^\circ}$ 0·9604, $n_D^{20^\circ}$ 1·489, acetyl value 125, and acid value 17, dissolved almost completely in dilute caustic alkali solution, whence 3% of resinous material was extracted by ether, and the phenolic constituent was liberated by passage of carbon dioxide.

Alternatively, the phenol was separated by extraction with ether after neutralisation of acid substances with an equivalent of alkali, or by acetylation and removal of acids by alkali extraction.

The ketonic phenol (*campnospermonol*) distilled at 260°/5 mm. with some decomposition as an amber, oily liquid that gave no distinctive coloration with ferric chloride; it had $d^{15\cdot5^\circ}$ 0·9454 and $n_D^{20^\circ}$ 1·4925 (Found: C, 81·2; H, 10·5. $C_{27}H_{42}O_2$ requires C, 81·4; H, 10·7%).

Campnospermonyl acetate had $d^{15\cdot5^\circ}$ 0·9550, $n_D^{20^\circ}$ 1·489, and b. p. 255—260°/5 mm.

Campnospermonol oxime distilled with some decomposition at 240°/5 mm.; $d^{15\cdot5^\circ}$ 0·9195; $n_D^{20^\circ}$ 1·489 (Found: N, 3·0%).

Campnospermonyl Methyl Ether.—Since the methyl ether was deemed best adapted for investigation, the bulk of the oil was methylated with methyl sulphate and sodium hydroxide, a small amount of acid material removed by hydrolysis of the ester and extraction of the alkali salt, and the residue distilled. The light yellow, oily *ether* distilled constantly at 240°/5 mm., appeared homogeneous, and had $d^{15\cdot5^\circ}$ 0·9342, $n_D^{20^\circ}$ 1·4960, iodine value 131, $[R_L]_D$ 128·8 (calc. for $C_{28}H_{44}O_2$, 128·8) (Found: C, 81·3; H, 10·7; OMe, 7·5.* $C_{28}H_{44}O_2$ requires C, 81·5; H, 10·7; OMe, 7·3%. $C_{29}H_{46}O_2$ requires C, 81·7; H, 10·8%).

The stable *oxime* had b. p. 215°/4 mm., $d^{15\cdot5^\circ}$ 0·9010, and $n_D^{20^\circ}$ 1·478 (Found: N, 3·2. $C_{29}H_{47}O_2N$ requires N, 3·2%).

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* On analyses alone, formulæ comprising 26 to 29 carbon atoms could not be excluded for campnospermonol and its derivatives.

Oxidation Products of Campnospermonyl Methyl Ether.—(a) The methyl ether (200 g.) in acetone (500 c.c.) at 0° was oxidised with potassium permanganate (440 g.). After removal of the acetone, which left no residue on evaporation, the manganese dioxide was repeatedly treated with boiling water, the solution of potassium salts concentrated to small bulk and acidified with dilute sulphuric acid, a considerable amount of volatile acid distilled in steam, and the residual liquor thoroughly extracted with ether, finally in a continuous extractor. All the acids were converted into ethyl esters and fractionally distilled.

The bulk of the esters (90 c.c.) of acids volatile in steam distilled at 96—98°/10 mm. and had the constants of ethyl nonoate, $d^{15\cdot5^\circ}$ 0·8700, $n_D^{20^\circ}$ 1·420, b. p. 222°/760 mm.; the recovered acid was identified as nonoic acid by the percentage of silver (40·8) in the silver salt, by formation of the characteristic barium nonoate, and by preparation of the amide (m. p. 99·5°). The nonoic ester recovered corresponded practically to one-third of the weight of the methyl ether.

Formic acid was detected by qualitative tests in the distilled acid liquor after extraction of nonoic acid with ether.

The esters of acids not appreciably volatile in steam were separated by fractionation (5 mm.) ultimately into two main fractions (i and ii), and a small first fraction consisting essentially of ethyl nonoate. (i) was ethyl *m*-methoxybenzoate (30 c.c.), b. p. 110°/5 mm., 255°/760 mm., $d^{15\cdot5^\circ}$ 1·082, $n_D^{20^\circ}$ 1·491. The liberated acid was identified as *m*-methoxybenzoic, m. p. 106·5° (Found : C, 62·8; H, 5·4; OMe, 20·1; Ag in silver salt, 41·6%). (ii) was ethyl azelate (40 c.c.), b. p. 130—132°/5 mm., 290°/760 mm. The recovered acid, crystallised from water, melted at 106·5° (Found : C, 57·6; H, 8·6; Ag in silver salt, 53·6; acid number, 592. Calc. : C, 57·5; H, 8·5%; acid number, 596).

(b) Campnospermonyl methyl ether (10 g.), dissolved in chloroform (50 c.c.), was treated with ozone in the usual manner, and the viscous ozonide, after removal of the chloroform in a vacuum, was decomposed by steam. Nonoaldehyde and nonoic and formic acids were readily identified products, the last-named by the usual qualitative reactions and formation of lead formate (Found : Pb, 70·1%). The products not volatile with steam consisted of aldehydic and acid material, non-crystallisable and non-distillable, and obviously complex, consisting apparently of an aromatic nucleus and considerable side chain. No simple aromatic acid or aldehyde appeared to have been formed : this fact, indicative of absence of complete scission of the molecule at the second ethenoid linkage, together with the production of formic acid was evidence of the presence of the attached methylene group in the chain.

The occurrence of nonoic and azelaic acids as oxidation products demonstrated the presence in campnospermonol of the unsaturated linkage of natural oleic acid.

Reduction Products of Campnospermonol.—(a) Three successive treatments with sodium and alcohol were required to complete the reduction of campnospermonyl methyl ether to the corresponding *secondary alcohol*, $d^{15\cdot5^\circ}$ 0·9191, b. p. 250°/5 mm. (Found : C, 80·9; H, 10·9. $C_{28}H_{46}O_2$ requires C, 81·1 ; H, 11·1%). The unsaturated linkages remained unaffected.

(b) Pure dry hydrogen was passed into a vigorously shaken solution of campnospermonyl methyl ether (50 g.) in anhydrous ether (200 c.c.) in which 0·25 g. of platinum dioxide was present (Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397). Saturation was rapid, and *hydrocampnospermonyl methyl ether* was isolated; it crystallised from alcohol in plates, m. p. 54° (Found : C, 80·9; H, 11·4. $C_{28}H_{48}O_2$ requires C, 80·8; H, 11·5%).

The crystalline *oxime* melted at 43° (Found : N, 3·1. $C_{28}H_{49}O_2N$ requires N, 3·2%).

The analytical values indicate addition of four hydrogen atoms to the molecule and the existence in campnospermonol of two ethenoid linkages. By similar reduction of campnospermonyl acetate there was obtained also wax-like *hydrocampnospermonyl acetate* (m. p. 61°; acetyl value 128), sparingly soluble in cold alcohol, from which crystalline *hydrocampnospermonol*, m. p. 70°, was obtained on hydrolysis.

(c) Reduction of campnospermonyl methyl ether with amalgamated zinc and concentrated hydrochloric acid (Clemmensen, *loc. cit.*) proceeded with extreme slowness at 100° even with constant and vigorous agitation. Addition of glacial acetic acid appreciably promoted the reaction. Treatment was continued during several days until, as apparent from the attainment of minimum density of the product, conversion of the carbonyl into the methylene group was complete. The ethenoid linkages were unaffected. The product was a colourless unsaturated *methoxy-hydrocarbon*, almost insoluble in alcohol, $d^{15\cdot5^\circ}$ 0·9093, $n_D^{20^\circ}$ 1·4950, b. p. 226°/5 mm. (Found : C, 84·2; H, 11·6. $C_{28}H_{46}O$ requires C, 84·4; H, 11·6%).

Further reduction with hydrogen in presence of platinum gave a saturated crystalline *methoxy-hydrocarbon*, m. p. 45° (Found : C, 83·2; H, 12·5. $C_{28}H_{50}O$ requires C, 83·6; H, 12·4%), which was stable to permanganate in boiling acetone.

The amount of these methoxy-hydrocarbons available did not permit of further examination.

Oxidation of Hydrocampnospermonyl Methyl Ether.—The reaction between the ether (50 g.) in acetone (200 c.c.) and potassium permanganate (157 g.), tardy in the cold, was completed in the boiling solution. After removal of the acetone the manganese dioxide was extracted with (*a*) boiling 90% alcohol and (*b*) boiling water.

(*a*) The potassium salt that separated on concentration and cooling was converted into ethyl ester, b. p. 185°/5 mm., m. p. 28° after recrystallisation. The acid obtained by hydrolysis and recrystallisation from alcohol and from acetone was margaric acid, m. p. 61·5°, acid number 204 (Found : C, 75·3; H, 12·5; Ag in silver salt, 28·8. Calc. : C, 75·5; H, 12·6%; acid number, 207).

(*b*) The aqueous extract, to which was added the mother-liquor from the crystallisation of potassium margarate, was acidified, and the acid extracted by ether was esterified and fractionally distilled. The principal fraction was ethyl *m*-methoxybenzoate with a little ethyl margarate. Oxalic acid was detected in the aqueous extract after removal of the liberated *m*-methoxybenzoic acid.

Reaction of Oximinohydrocampnospermonyl Methyl Ether with Phosphorus Pentachloride.—Hydrocampnospermonyl methyl ether (20 g.), suspended in absolute alcohol (200 c.c.) in which sodium (3 g.) was dissolved, was shaken at 0° with amyl nitrite (15 g.) for several hours. The liquor was then diluted with water, filtered, and treated with acetic acid, an imperfectly crystalline oximino-compound (20 g.), apparently a mixture, being thus obtained. This, in dry chloroform (50 c.c.) at 0°, was treated with phosphorus pentachloride (15 g.) and after several hours the chloroform solution was washed with water and extracted with dilute aqueous potassium hydroxide. The acid yielded by the alkaline solution was converted into an ethyl ester, m. p. 33° after recrystallisation from alcohol; the acid recovered from this was stearic acid, m. p. 69°, acid number 197 (Found : C, 75·8; H, 12·5. Calc. : C, 76·0; H, 12·7%; acid number, 197).

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