The Constitution of Campnospermonol.

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The examination of the oily exudate from *Campnospermum brevipeoliolatum* a large tree endemic in the Sepik River district, Mandated Territory of New Guinea, was undertaken by Jones and Smith and the result of their investigation published in the Journal of the Chemical Society in 1928. It was shown, as a result of that investigation, that the principal constituent of the exudate was a ketonic phenol to which the name, campnospermonol, was given and a tentative formula was suggested for this substance. The investigation has now been continued by the present author, further supplies of the exudate having become available through the courtesy of Father Kirschbaum of the Sepik River Mission Station. It has been found possible to assign a definite constitution to the substance and it is to be represented as of molecular composition, \( C_{25}H_{40}O_2 \), with the following constitution—

\[
\text{HO} \left( \text{CH}_2\text{CO} \left( \text{CH}_2 \right)_7 \text{CH:CH} \left( \text{CH}_2 \right)_7 \text{CH}_3 \right)\]

\( \alpha \text{--} m \text{--} \text{hydroxyphenyl} -- \Delta \chi -- \text{nonadecen} -- \beta \text{--} \text{one}. \)

This constitution differs from that originally proposed by Jones and Smith from the incomplete data at their disposal, in containing only one double linkage and in molecular composition, \( C_{27}H_{42}O_2 \), or \( C_{28}H_{44}O_2 \), being originally proposed.

As recorded in the original paper, accidental loss of the nitrile portion resulting from the decomposition of oximinohydrocampnospermonyl methyl ether with phosphorus pentachloride, prevented determination of the constitution of this nitrile which, along with data already obtained, furnished the key to the structure of the phenolic ketone. This nitrile has now been obtained and proved to be \( m \)-methoxy phenyl cyanide, the acid derived from it on hydrolysis being \( m \)-methoxy benzoic acid. The products obtained from the above decomposition are \( m \)-methoxy phenyl cyanide and stearic acid whence it follows that hydrocampnospermonyl methyl ether is to be
represented as;

$$\text{CH}_3\text{O} \quad \text{CH}_2\text{CO(CH}_2)_{16}\text{CH}_3$$

with campnospermonyl methyl ether represented by,

$$\text{CH}_3\text{O} \quad \text{CH}_2\text{CO(CH}_2)_7\text{CH:CH(CH}_2)_7\text{CH}_3$$

As a further confirmation, the oximino derivative of campnospermonyl methyl ether itself has been prepared and similarly decomposed with phosphorus pentachloride, the products in this case being m-methoxy phenyl cyanide and oleic acid.

A careful determination of the iodine value of campnospermonyl methyl ether and campnospermonyl acetate purified as far as possible, gave values 80 and 66 respectively. The theoretical values for one double bond are 65 and 60 and it is clear that the value 80 is somewhat high. No explanation of this inconsistency in the values of the methyl ether and acetate is apparent but it is probably to be found in the presence of some substance or substances occurring along with the campnospermonol in the oil, possibly the small amount of acid indicated by the acid number 17 of the original exudate.

Analyses of the methyl ether, the hydro-methyl ether and the alcohol obtained by reducing the ketone group in the hydro-methyl ether have been again carried out with results consistent with the respective formulae now suggested for these substances. The oxidation products of campnospermonyl methyl ether have been again examined and suberic acid isolated as a product additional to those already reported, namely, azelaic, nonoic and m-methoxy benzoic acids. It also seems clear that the oxidation product of hydrocampnospermonyl methyl ether previously described as margaric acid, is really a mixture of that acid with some stearic acid, a result in accordance with the constitution assigned.

It is hoped to publish an account of further derivatives of campnospermonol at a later date.

**Experimental.**

**Combustion results.**

**Campnospermonyl methyl ether.**

Found $C = 80.6$, $H = 10.7$.

$(C_{26}H_{42}O_2$ requires $C = 80.8$, $H = 10.8$).

**Hydrocampnospermonyl methyl ether.**

Found $C = 80.4$, $H = 11.4$.

$(C_{26}H_{44}O_2$ requires $C = 80.4$, $H = 11.5$).

**Hydrocampnospermonyl methyl ether.**

Found $C = 79.9$, $H = 11.6$.

$(C_{26}H_{46}O_2$ requires $C = 80.0$, $H = 11.8$).

**Reaction of oximino campnospermonyl methyl ether with phosphorus pentachloride.**
Fifty grammes of campnospermonyl methyl ether were added to 200 ccs. absolute alcohol in which 3 grammes of sodium had been dissolved and after cooling to 0°C, 20 ccs. of amyl nitrite were slowly added and the mixture maintained at 0°C for 4 hours. The liquid was then diluted with water and extracted thoroughly with petroleum ether. The alkaline extract remaining, was acidified with dilute sulphuric acid and the oximino derivative which separated, isolated by ether extraction. It was then dissolved in dry chloroform, cooled to 0°C and finely powdered phosphorus pentachloride slowly added till no further reaction took place. Ice was then added and the chloroform solution removed. Evaporation of the chloroform gave a liquid which was separated into (a) a nitrile, (b) an acid, by treatment with dilute sodium hydroxide and ether extraction.

(a) The nitrile was distilled in vacuo and the distillate solidified on cooling. Hydrolysis gave a good yield of m-methoxy benzoic acid M.P. 106.5°C.

Found C = 62.9. H = 5.1.

(C₈H₇O₂ requires C = 63.1. H = 5.2).

(b) The acid was converted into its methyl ester and fractionated. The iodine value for the distilled ester was 85. (Theor. for methyl oleate = 87).

Identity with methyl oleate was confirmed by oxidation with permanganate in acetone solution. Nonoic and azelaic acids being identified as the products.

In a similar reaction with hydrocampnospermonyl methyl ether, m-methoxy benzoic acid and stearic acid were obtained.

**Oxidation of hydrocampnospermonyl methyl ether.**

Examination of the ethyl esters obtained in this oxidation by methods already described (loc. cit.) resulted in the isolation of a small fraction of ethyl suberate as a fraction boiling a little below that of the main fraction, ethyl azelate, obtained on fractionation.

Hydrolysis gave suberic acid M.P. 132°C.


Acid Number = 635.

(C₈H₁₄O₄ requires C = 55.1. H = 8.1).

**Oxidation of hydrocampnospermonyl methyl ether.**

The fatty acid isolated in this oxidation and previously described as margaric acid was again examined. The acid number was carefully determined and the molecular weight calculated, the value 274 being obtained as a result of several determinations. The molecular weight of margaric acid is 270 and that of stearic acid 284 and it is clear that margaric acid is the principal product but mixed with about 30% stearic acid. The melting point of the sample was determined as 57.5°C.

**REFERENCE**
