Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

identification of the carotinoids of different plants. As Zopf[1] justly says careful macro-chemical investigation alone can lead to decisive results in such cases.

Chemistry. — *"Equilibria in ternary systems I"*. By Prof. F. A. H. Schreinemakers.

(Communicated in the meeting of October 26, 19.2).

On the equilibria occurring in ternary systems between liquid and vapour different theoretical[2] and experimental[3] investigations have already appeared previously. We will now discuss a few cases where, in addition to liquid and vapour, solid substances occur also.

The system $F L G$.

We choose for F a ternary compound and will assume that the three components occur in the vapour.

We now choose at a definite constant temperature T such a pressure P that no vapour can form. The isotherm can then consist only of the saturation line of the solid substance F. This saturation line is a closed curve surrounding the point F like the closed curve of Fig. 1, for instance.

On reduction of P a gas region appears somewhere and at the same time a heterogeneous region separating the gas region from the liquid region. In Fig. 1 the gas region is indicated by G, the liquid-region by L ; the drawn line is the liquid-line, the dotted one the gas- or vapour line of the heterogeneous region. The straight lines drawn in this heterogeneous region unite the liquids with the vapours with which they can be in equilibrium.

We now have in Fig. 1 two homogeneous regions, namely the liquid region L and the gas region G ; in addition we find two heterogeneous regions.

In one of them a mixture dissociates into L + G ; we will call

[1] W. Zopf, Zur Kenntnis der Färbungsursachen niederer Organismen (Dritte Mitteilung), Beiträge zur Physiol. u. Morph. niederer Organismen, 1892, Erstes Heft, p. 36.

[2] J. D. van der Waals. These Proc. Vol. IV p. 448, 539, 681; Vol. V p. 1, 121, 225. (1902).

F. A. H. Schreinemakers. Zeitschr. f. phys. Chem. 36 257, 413, 710 (1901) 37 129 (1901) 38 227 (1901) 43 671 (1903)

B. M. van Dalfsen. Dissertation, Amsterdam. (1906).

[3] F. A. H. Schreinemakers. Zeitschr. f. Phys. Chem. 39 485, 40. 440, 41. 331 (1902), 47 445, 48 257 (1904).

B. M. van Dalfsen. l.c.

this the heterogeneous region LG. In the other takes place a dissociation into solid F and a liquid saturated with F of the saturation line of F; we will call this the heterogeneous region FL.
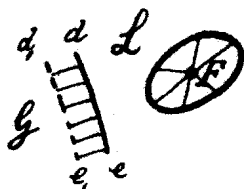

Fig. 1.

If we imagine the liquid- and vapour surface of the ζ-surface to be introduced above Fig. 1, it is obvious that the solid substance F can be also in equilibrium with a whole series of ternary vapours, which equilibria, however, are in the present case all metastable yet. It is also obvious that these vapours must form in Fig. 1 a closed curve surrounding point F, which curve, however, has been omitted from the figure. We will call this curve "vapour saturation curve" of the solid substance F. This curve surrounds the heterogeneous region FG which, however, is still quite metastable.

Hence in Fig. 1 we distinguish :

the saturation line of F.

the vapour saturation line of F (metastable).

the vapour- and liquid-line of the heterogeneous region L G.

the vapour region (G) and the liquid-region (L.)

and the heterogeneous regions L G, L F and G F, the latter of which is metastable.

The vapour region G can form within as well as without the saturation line of F; on further reduction of the pressure there may occur also several vapour regions first isolated from each other and afterwards amalgamating. Moreover, in the system liquid + gas there may occur either binary or ternary vapour pressure maxima or minima or stationary points so that different cases are to be distinguished. We will first take the case that there occurs neither a binary or ternary maximum or minimum nor a stationary point so that the gas region appears in one of the apexes of the component-triangle and the liquid region disappears in one of the other apexes.

In Fig. 1 the gas region is, therefore, formed outside the saturation line of F; on reduction of the pressure, the different curves of Fig. 1 will change in form and position. As a rule, a small change in pressure only causes an exceedingly small change in the solubility of a solid substance; hence, the saturation line of F will alter but little on change of pressure within very wide limits. This, however, as we will notice presently, becomes different when we get near to the melting point of F so that the saturation line of F is only still a small curve.
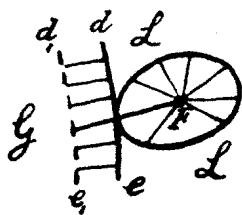
Fig. 2.

The influence of a change in pressure on a liquid and vapour region is, however, great in comparison with that on the saturation line of F. When the pressure decreases, the gas region extends and the liquid region contracts; the heterogeneous region L G shifts, therefore, in Fig. 1 towards the heterogeneous region FL. Hence, on reduction of pressure, there will occur a pressure as represented in Fig. 2 where the liquidline and the saturation line of F will meet in a point M so that the equilibrium $F + L_M + G_{M_1}$ appears. The three points F, M, and M_1 as follows readily from the indicatrix theorem, are situated on a straight line. With the aid of the two sheets of the ζ-surface it is also easy to see that the non-drawn vapour saturation line of F in Fig. 2, must meet the vapour line in M_1.
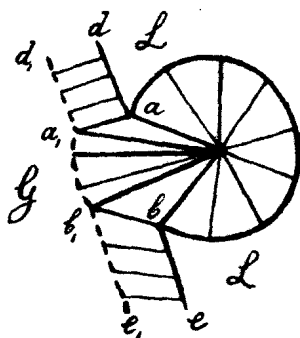

Fig. 3.

On further decrease of the pressure, the saturation line of F and the liquidline intersect each other in two points; these intersecting points are represented in Fig. 3 by a and b; in the solid substance the letter F is omitted.

From a contemplation of the liquid sheet and vapour sheet of the ζ-surface it follows at once that with each intersecting point of the saturation line of F and the liquidline is conjugated an intersecting point of the vapour saturation line of F and the vapour line. As the saturation line of F and the liquidline intersect each other in the points a and b, the vapour saturation line of F and the vapour line must intersect each other in the two points a_1 and b_1. The curve a_1 b_1 is the vapour saturation line of F, the vapour line consists of the two parts e_1 b_1 and a_1 d_1 which are, of course, connected with a metastable branch not drawn in the figure.

At the pressure contemplated here, two three-phase equilibria $F + L + G$ therefore occur, namely:

$$F + L_a + G_{a_1} \text{ and } F + L_b + G_{b_1}$$
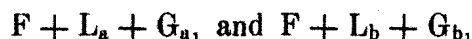
On further reduction of the pressure, the heterogeneous region L G shifts more and more in such a direction that the vapour region becomes larger and the liquid-region smaller. At a certain pressure, the liquidline will pass through the point F, after which this gets situated within the heterogeneous region. We then obtain an isotherm as in Fig. 4 which does not differ essentially from that of Fig. 3.

On further decrease of the pressure, the points a and b and consequently a_1 and b_1 will at a definite pressure coincide; here we first assume that F then still lies within the heterogeneous region LG. We then obtain an isotherm like in Fig. 5 in which we must
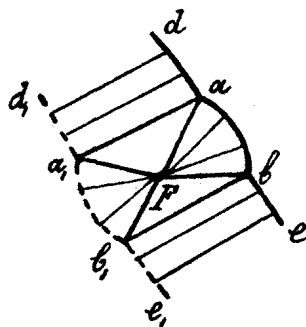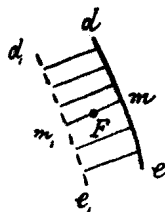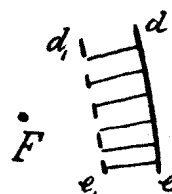

Fig 4.   Fig. 5.   Fig. 6.

imagine m to be formed by the coincidence of a and b, and m_1 by the coincidence of a_1 and b_1. It is obvious that m_1, F and m must lie on a straight line and that the non-drawn and metastable saturation line of F must meet the curve d e in m and that the vapour saturation line of F must meet the curve d_1 e_1 in m_1.

On further decrease of pressure the saturation and vapour saturation curves of F arrive quite within the heterogeneous region L G; F cannot, therefore, occur any longer in the solid condition but splits into vapour + liquid; the compositon of the vapour is now represented by a point of the vapour line d_1 e_1, that of the liquid by a point of the liquidline d e. Both points lie with F on a straight line.

On reducing the pressure still further we obtain, when the gas region has extended itself over the point F, isotherms like those in Fig. 6. The vapour saturation line of F has now disappeared, the saturation line of F can, however, still exist but then represents only metastable solutions and has, therefore, been omitted from the figure.

From the foregoing views, it now follows at once that the liquid as well as the vapour of the system F + L + G trace a closed curve, like in Fig. 7 and that on each of these lines occurs a point of maximum and of minimum pressure. As the points of the curves of Fig. 7 all appertain to a same temperature but to different pressures, we may call Fig. 7 an isothermic — polybaric diagram.
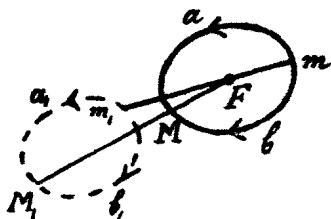
Fig. 7.

The curve M a m b represents the solutions which, at a given temperature are saturated with F under their own pressure; the compositions of the vapours are indicated by the curve M_1 a_1 m_1 b_1. We may, therefore, call the curve M a m b, the isothermic saturation line of F under its own vapour pressure and M_1 a_1 m_1 b_1 its conjugated vapour line; where no mistake is possible we will omit the adjunct "isothermic".

As a rule, the saturation line of F at a certain constant pressure P and the saturation line of F under its own vapour pressure will differ but little, so that, practically, we may substitute the one for the other; as to exceptions for temperatures in the vicinity of the melting point of the compound F to them we will refer later.

We have already stated above that the saturation line of F, under its own vapour pressure, must exhibit a point with a vapour pressure maximum and another with a vapour pressure minimum; the first is represented in Fig. 7 by M, the second by m. On the conjugated vapour line, there occur, of course also two points M_1 and m_1 of which M_1 represents the vapour with the vapour pressure maximum and m_1 that with the vapour pressure minimum. The arrows on both curves indicate the direction of the increasing vapour pressure.

The points F, M and M_1 are, of course, situated on a straight line and agree with the isothermic-isobaric diagram of Fig. 2; the points F, m and m_1 which are of course also situated on a straight line, agree with the isothermic-isobaric diagram of Fig. 5.

We have assumed above that on lowering the pressure the diagrams 3, 4 and 5 succeed each other, or in other words that the points a and b of Figs. 3 and 4 had already coincided in a point m of Fig. 5 before the vapour region had extended to over F. If, however, the vapour line has already passed point F before a and b of Fig. 3 or 4 coincide we get an isotherm as in Fig. 8 which, however, does not differ essentially from Fig. 3 or 4. On further reducion of the pressure Fig. 8 is converted into Fig. 9. The vapour saturation line of F now meets the vapour line e_1 d_1 in m_1; the saturation line of F not drawn in Fig. 9 meets the liquidline e d in m. The vapour saturation line of F represents the stable, the saturation line of F the metastable conditions. The points F, m and m_1 are, of course, again situated as in Fig. 5 on a straight line; as, however, these points are situated, in the two figures, differently in regard to each

other, the reaction between solid F, liquid m and gas m_1 is in these two cases also different.
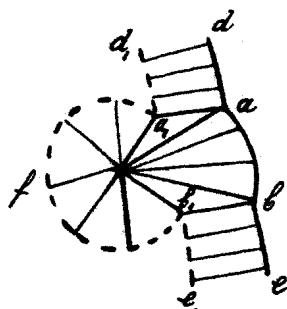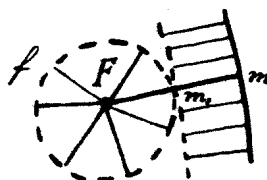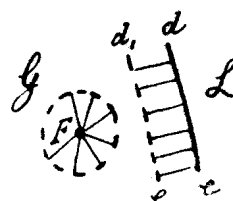

Fig. 8.   Fig. 9.   Fig. 10.

On reducing the pressure still further, the two regions L G and F G separate and diagrams as in Fig. 10 are obtained. The non-drawn saturation line of F represents metastable conditions only; solutions saturated with F can, therefore, occur only in the metastable condition at this pressure.
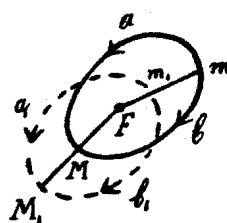

Fig. 11.

The case is, however, different with the vapours saturated with F; these all occur in the stable condition and are represented by the closed vapour saturation line of Fig. 10.

By a further fall in pressure this vapour saturation line of F becomes continuously smaller; at the vapour pressure of the compound F it contracts to a point, namely point F, and on further reduction in pressure it disappears.

Hence, the liquid as well as the vapour of the system F + L + G again trace a closed curve (Fig. 11). M a m b is the saturation line of F under its own pressure, M_1 a_1 m_1 b_1 its conjugated vapour line. On the one curve the pressure in M is maximum and in m minimum, on the other curve in M_1 and m_1; the pressure thus increases in both in the direction of the arrows.

The two Figs. 7 and 11 exhibit a great resemblance to each other; yet they differ in different respects such as for instance, in the situation of the points F, m and m_1 in regard to each other. This causes that in Fig. 7 the point F is situated outside and in Fig. 11 within the vapour line.

When deducing the previous diagrams we have assumed that on change of pressure, the liquidline of the heterogeneous region moves more rapidly than the saturation line of F or what amounts to the same that the vapour line of the heterogeneous region L G moves quicker than the vapour saturation line of F.

Although this is the case generally, it no longer holds good if we take a temperature close to the melting point of F. The saturation line of F then surrounds a comparatively small region which on change of pressure, can rapidly extend, or possibly contract. The saturation line of F will then move more rapidly than the liquid-line of the region L G. We will now distinguish two cases in one of which the substance expands on melting whilst in the other case it contracts.

F expands on melting. An increase in pressure (at constant T) will cause a solidification of the molten F, a decrease in pressure a fusion of solid F. On decrease in pressure, the isothermic saturation line of F will consequently contract rapidly and disappear in the point F. We now start from Fig. 1 and assume that, on lowering the pressure, the saturation line of F contracts at first rather slowly and then more rapidly; its movement is more rapid than that of the liquid line of the heterogeneous region L G.

If now the movement of the saturation line of *F* is slower than that of the liquid line, Fig 1 may be converted into Fig. 2 and then into Fig. 3 from which are then formed either the Figs. 4, 5 and 6 or the Figs. 8, 9 and 10. If however, after the isotherms have assumed a form as in Fig. 3, the movement of the saturation line becomes more rapid than that of the liquidline, then, after the appearance of the isotherms of Fig. 3, those of Fig. 2 and 1 reappear. On reduction of the pressure we then get a series of isotherms such as:

fig. 1 → fig. 2 → fig. 3 → fig. 2a → fig. 1a

in which the figures occurring after fig. 3 are indicated by 2a and 1a. Fig. 2 and 2a resemble each other with this great difference, however, that in fig. 2a the saturation line of F is much smaller and that the liquid and vapour lines of the heterogeneous region lie more adjacent to F than in fig. 2. The same applies to fig. 1a in regard to fig. 1. Between fig. 2 and 2a there is also still this difference that Fig. 2 applies to the maximum and Fig. 2a to the minimum pressure of the system F + L + G. We will therefore assume that in fig. 2a the letters M_1 and M of fig. 2 have been replaced by m_1 and m.
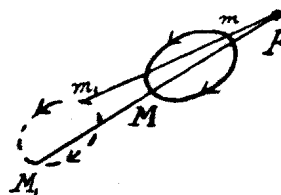

Fig. 12.

From the previous considerations it now follows at once that the saturation line of F under its own vapour pressure must be situated as in fig. 12; contrary to this same curve in fig. 7 and 11 it does not surround the point F which represents the solid phase with which its solutions are saturated. We will, therefore

call the saturation line of F in figs. 7 and 11 a circumphased and that of fig. 12 an exphased one.

F contracts on melting. An increase in pressure (at constant T) will, therefore cause a fusion of solid F, a decrease of pressure a solidification of molten F. On decrease of pressure the isothermic saturation line of F will consequently form first of all in F and then extend at first rapidly and then slowly.

We now start from such a pressure that a heterogeneous region L G does exist, but not yet the saturation line of F. We then have fig. 1 from which we must, however, leave out the saturation line of F. On lowering the pressure, the liquid line shifts towards F and we assume that it has already just passed the point F when the saturation line of F appears in the point F. The isotherm then has a form as in fig. 5 or 6 in which, however, we must assume the curve d e to be very close to F. On further reduction of pressure the saturation line of F now rapidly extends round the point F and overtakes the liquid-line so that at a definite pressure they come into contact with each other. We then obtain an isotherm as in fig. 5 or 9. In fig. 5 however, we must imagine the saturation and the vapour saturation lines of F to be drawn and in such a manner that the first curve comes into contact with e d in m, the second curve with d_1 e_1 in m_1. In Fig. 9 we must also imagine the saturation line of F coming into contact with the curve d e in m.

On further reducing the pressure fig. 4 or 8 are formed and as the velocity of the saturation line of F now becomes smaller than that of the liquid-line, these are again converted into fig. 5 or 9. Hence on reduction of pressure we obtain a succession of isotherms such as :

fig. 5 → fig. 4 → fig. 5a or fig. 9 → fig. 8 → fig. 9a.

in which fig. 5a differs from fig. 5, and fig. 9a from fig. 9 in this way, that in the figures indicated by a the liquid line e d is removed further from point F. Also, as the fig. 5 and 9 occur at higher pressures than the fig. 5a and 9a the letters m and m_1 must be considered as being replaced by M and M_1.
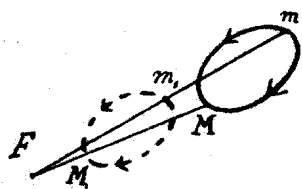

Fig. 13.

From these considerations it now follows that the saturation line of F must exist under its own pressure as in fig. 13, hence exphased; the correlated vapour line may be exphased as well as circumphased and may also be situated on the other side of F.

The case may also occur that the satu-

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ration line under its own pressure and its correlated vapour line get each reduced to a point. Both these points then lie with F on a straight line.

This case will occur when the saturation line of F and the liquid line when meeting each other in a point (fig. 2 in M, in fig. 5 and 9 in m) move at that moment from that point towards and from F with the same velocity. The same then applies to the vapour line and vapour saturation line of F which also meet in a point (M_1 in fig. 2 and m_1 in fig. 5 and 9). This equality of velocity has, of course, also a physical significance, which we will look for.

We represent the composition and the volume of the solid substance F by α, β and v, that of the liquid by x, y and V and that of the gas by $x_1 y_1 V_1$.

The equation of the saturation line of F is then given by:

$$[(\alpha - x) r + (\beta - y)s] \, dx + [(\alpha - x) s + (\beta - y) t] \, dy = - \Delta V . dP \quad (1)$$

and that of the liquid line of the heterogeneous region LG by:

$$[(x - x_1) r + (y - y_1) s] \, dx + [(x - x_1) s + (y - y_1) t] \, dy = V_{0.1} \, dP \quad (2)$$

in this:

$$\Delta V = V - v + (\alpha - x) \frac{\partial V}{\partial x} + (\beta - y) \frac{\partial V}{\partial y}$$

$$V_{01} = V - V_1 + (x_1 - x) \frac{\partial V}{\partial x} + (y_1 - y) \frac{\partial V}{\partial y}$$

As the two curves (1) and (2) come into contact with each other x and y in (1) and (2) are the same and then we have:

$$\frac{\beta - y}{\alpha - x} = \frac{y_1 - y}{x_1 - x} = \frac{\beta - y_1}{\alpha - x_1} = \mu.$$

If now we write (1) and (2) in the form:

$$(r + \mu s) \, dx + (s + \mu t) \, dy = - \frac{\Delta V}{\alpha - x} \, dP$$

$$(r + \mu s) \, dx + (s + \mu t) \, dy = \frac{V_{0.1}}{x - x_1} \, dP$$

we notice that the above mentioned circumstance will appear as:

$$- \frac{\Delta V}{\alpha - x} = \frac{V_{0.1}}{x - x_1}.$$

After substitution of the values ΔV and $V_{0.1}$ we can write for this also:

$$(\alpha - x_1) V + (x - \alpha) V_1 + (x_1 - x) v = 0$$

or $\quad (\beta - y_1) V + (y - \beta) V_1 + (y_1 - y) v = 0.$

This means that the change in volume which can occur in the reaction between the three phases *F*, *L*, and *G*, which are in equi-

librium with each other is *nil.* The reaction between the three phases therefore takes place without a change in volume. We will return to this later.

We may summarise the above as follows:

The isothermic-isobaric saturation and vapour saturation curves of a solid substance F are, at all temperatures and pressures, circumphased and disappear (are formed) in the point F.

The saturation curves of a solid substance F under their own vapour pressure are at a lower temperature circumphased; at a definite temperature, one of them passes through the point F after which, at higher temperatures, they become exphased, then they disappear in a point, if in the reaction between the three phases no change of volume occurs. This also applies to the vapour lines appertaining to the saturation lines under their own pressure which can, however, be already exphased at lower temperatures.

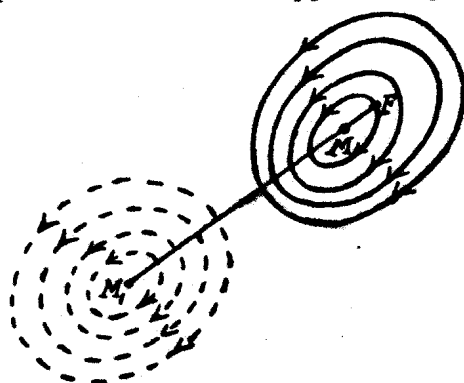In fig. 14 are drawn some saturation lines under their own vapour pressure with their appertaining vapour lines for different temperatures. On each of these curves occurs a point with a maximum and one with a minimum vapour pressure which, however, are not indicated in the Fig. although the arrows indicate the directions in which the pressure increases. These points are situated of course, in such a manner, that the line which unites two points with a maximum or minimum pressure of curves of the same temperature, passes through the point F. The saturation line under its own vapour pressure disappears in the point M; the appertaining vapour-line in the point M, both points lie with F on a straight line.

Fig. 14.

In fig. 14 the curves of different temperatures are all united in a plane; if, however, we imagine a temperature axis drawn perpendicular to this plane and also the curves in space according to their temperatures, two surfaces are formed, namely the saturation surface, under its own pressure of F and the appertaining vapour surface. The first has its top in M, the second in M_1; the line MM_1 is situated horizontally. It is evident that the point F does not coincide with the top M of the saturation surface under its own vapour pressure but is situated somewhat lower and that the points M_1 M and F lie in a same vertical plane. (*To be continued*).

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Botany. — *"Dichotomy and lateral branching in the Pteropsida"*.
By Mr. J. C. SCHOUTE. (Preliminary communication). [1])

(Communicated in the meeting of Oct. 26, 1912).

In 1900 and more recently [2]) JEFFREY argued that the correspond-
ence in structure of Filicales, Gymnosperms and Angiosperms jus-
tified the union of these three groups into a higher group, that of
the Pteropsida.

Palaeontological research has later rendered this conclusion more
probable [3]).

When on this account we assume a closer relationship between
these groups, there naturally still remain many great differences
between them; one of these is in the method of branching. For
whilst the Gymnosperms and Angiosperms without exception branch
by means of axillary buds (apart from adventitious buds), we find
the ferns are typically dichotomous [4]). METTENIUS [5]) described long
ago in ferns lateral buds in every kind of position (axillary,
next to the insertion of the leaf, under the insertion, half on the
stem and half on the petiole) but all this has been explained by
VELENOVSKY as due to the formation of "stable adventitious buds [6]).
The distinction between dichotomy and lateral branching has always
been considered by all writers to be of great phylogenetic importance.

An investigation on branched tree-ferns has led me to the idea
that there may perhaps be no difference in principle between these
various modes of branching; in other words, that dichoto-
mous branching would be, in its essence, the same as the lateral
branching of ferns or Angiosperms. The fine material, mostly col-
lected by Mr. KOORDERS, on which this investigation has been made,
will be described exactly in the detailed publication. Here I only
remark that in these trees ordinary dichotomy can sometimes take
place, as a reaction to certain pathological processes, with a normal

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[1]) A detailed paper, illustrated by plates, will appear on this subject in the Recueil
des Travaux botaniques néerlandais.

[2]) E. C. JEFFREY. The Morphology of the Central Cylinder in the Angiosperms;
Canadian Inst. Trans., Vol. 6, 1900. — The Structure and Development of the
Stem in the Pteridophyta and Gymnosperms; Philos. Trans. R. Soc. London, Vol.
195, 1902.

[3]) See e. g. D. H. SCOTT, Studies in fossil. Botany, 2nd Ed. London 1908/09,
p. 638.

[4]) J. VELENOVSKY. Vergleichende Morphologie der Pflanzen. Prag 1905, p. 245.

[5]) G. METTENIUS. Ueber Seitenknospen bei Farnen, Abhandl. math-phys. Classe
k. Sächs. Ges d. Wiss. Bd. 5, 1861, p. 611.

[6]) l.c. p. 247.