

## 薬学博士柴田承二君の「或種の菌類及び地衣類の代謝生産物

### の研究」に対する授賞審査要旨

菌類及び菌と藻との共生体の地衣類は多種多様の代謝産物を生産する。柴田承二君は一九三八年以来朝比奈泰彦教授の協力者として地衣成分の研究に参加したが、一九四四年以降は独立してこの研究を継承し、それ等成分の化学構造の解明により、地衣の化学的分類 (Chemotaxonomy) に寄与すると共に、地衣の第二次代謝成分が、主としてその菌共生体に基因するとの見地から、更に数種の菌の代謝生産色素類の研究を展開し、それ等の化学構造を決定する事により、フェノール性単量体が二量化を伴って生成したと考え得る数系統の天然産色素類の存在を明らかにし、且つその一部ないしこれ等と生合成的に近親とみなし得る新地衣成分の存在を明らかにした。これ等の地衣及び菌成分は、その生合成機構を検討するに適した構造を持っており、その一部につきアイソトープ標識法を用い解明した。その内容は前後百余編に達する報文に包含されているが、主な成果は次の如くである。

一、*Penicillium islandicum* (イヌランゲア黄変米菌)並びに関連する菌の代謝産物として Chrysophanol, Islandicin, Emodin,  $\omega$ -Hydroxyemodin 及び Catenarin の五種の Oxyanthraquinone 単量体と、それ等が 8,8'-位で結合したすべての組合せを含む一二種の bis-Anthraquinone 体、これ等から誘導されたとみなし得る八種の変形 bis-Anthraquinone 体及び含窒素成分として Erythroskyrine を純粋に分離し、それ等の構造を Fig. 1 に示すが、こ

く決定した。なほこの内 (+)Skyrin と (+)Rugulosin とは地衣 *Acrocyphus sphaerophoroides* (カニムコウ) の成分としても発見された。又地衣 *Usnea bayleyi* からこれ等 bis-Anthrquinone 系中間体のB環の開裂によって生成されたものとみなし得る構造の三種の変形 bis-Xanthone 系色素 Eumitrin A<sub>1</sub>, A<sub>2</sub> 及び B を発見した (Fig. 2)。*Penicillium islandicum* はじつゆのイヌランチア黄変米の主要な原因菌で、(一) Luteoskyrin がその肝硬変毒性の本体の一つなる事、又その他の *Penicillium* 属の菌に広範に含まれる (+)Rugulosin も同様の毒性を有することが、小林、浦口、斎藤、辰野等の研究グループによって明らかたされている。

二' *Ustilaginoida virens* 及び *Fusarium culmorum* なる菌の代謝産物として三種の bis-Naphthopyrone 系色素を純粋に分離し、それ等の構造を Fig. 2 に示すごとく決定した。この内三種の Ustilaginoidin 及び前記の一二種の 8,8'-bis-Anthrquinone 系色素は皆不斉炭素有せむるにもかかわらず光学活性で、この種の廻転障害によるアトロプ異性体が天然にも存在する事を明らかにした最初の化合物群である。

三' *Penicillium duclauxii* なる菌の代謝産物として五種の変形 bis-Phenalenone 系色素を純粋に分離し、それ等の化学構造を決定した (Fig. 2)。又本菌を <sup>14</sup>C-養酸、<sup>14</sup>C-酢酸、<sup>2-<sup>14</sup>C</sup>-酢酸及び <sup>14</sup>C-マロン酸エステルで培養して得られる放射性 Duclauxin の分解により放射性炭素の分布を検討し (Fig. 2)、生成成機構が Fig. 3 に示すごとくなるべき事を明らかにした。

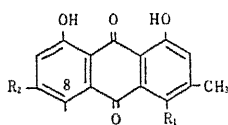
四' *Usnea*, *Parmelia* 及び *Cladonia* 属の新鮮な地衣体を用い、<sup>14</sup>C-標識の酢酸塩、養酸塩、マロン酸エステル、Methylphloracetophenone, Phloracetophenone 等を投与して <sup>14</sup>C の Usnic acid への取込みを検討し、Fig. 3 に

示すごとき生合成機構がある事を明らかにした。この際中間の Methylphloracetophenone の酸化的二量体がビドロフラン体に閉環する方式により異性体の生成が予想されるが、事実従来見落されていた Usnic acid なる新異性体の副生を証明した。Isousnic acid は *Cladonia* 属の地衣に存在が証明されるに至った。又同様の  $\alpha$ -C<sub>10</sub> 取込みの実験により、Usnic acid の生合成が冬に著しく盛になる事実を証明した。又地衣体の子器を用い、その菌共生体を純粋培養する簡単な方法を工夫し、*Parmelia crassa* 等の菌共生体の純培養により好収量で (+)Usnic acid が生成する事を証明した。

五、*Peltigera* 及び *Loburia* 属の地衣からそれぞれ Phlebic acid A と B 及び Retigeric acid A と B なる酸を分離し、それ等の構造決定によりおのおの Hopane 型及び Fernane 型骨格の Triterpenoid なる事を明らかにした (Fig. 4)。又 *Lobaria* 属地衣から分離される Retigeranic acid の構造が新しい骨格を有する Sesterterpenoid なる事を決定し (Fig. 4)、Sesterterpenoid が地衣成分としても存在する事を始めて明らかにした。

これ等の柴田君の研究業績は国際的に高く評価され、一九六六年英国化学会の百年記念会講演者として、又今年二月ニューデリーの国際純粋応用化学連合 (IUPAC) の第八回天然物有機化学討論会の特別講演者として招待され、又一九七三年九月ハンブルクにおける第二四回 IUPAC 大会の天然物部会招待講演者に予定されている。なお一九六九年レオポルチナ・ドイツ自然科学者アカデミー会員に選定され、又一九六八年以来 IUPAC の協議会で再度にわたり理事に選出され、国際的に大いに活躍している。

Fig 1

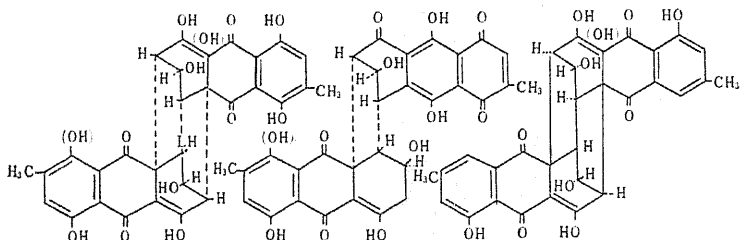


- |                 |   |
|-----------------|---|
| $R_1=R_2=H$     | Chrysophanol (Ch)   |
| $R_1=OH, R_2=H$ | Islandicin (Is)   |
| $R_1=H, R_2=OH$ | Emodin (Em)   |
| $R_1=R_2=OH$    | Catenarin (Cat)   |
| $R_1=H, R_2=OH$ | $CH_3$ の代わりに $CH_2OH$ $\omega$ -Hydroxyemodin<br>( $\omega-OH-Em$ ) |

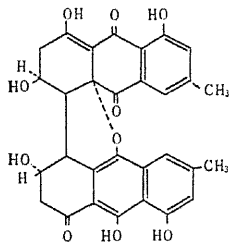
8,8'-Bisanthraquinone 系

- |                                      |                                  |
|--------------------------------------|----------------------------------|
| (+) Dianhydrorugulosin (2 Ch)        | (+) Iridoskyrin (2 Is)           |
| (+) Skyrin (2 Em)                    | (+) Dicatenarin (2 Cat)          |
| (+) Roseoskyrin (Ch + Is)            | (+) Auroskyrin (Ch + Em)         |
| (+) Rhodoislandin A (Ch + Cat)       | (+) Rhodoislandin B (Em + Is)    |
| (+) Punicoskyrin (Is + Cat)          | (+) Aurantioskyrin (Em + Cat)    |
| (+) Oxyskyrin (Em + $\omega-OH-Em$ ) | (+) Skyrinol (2 $\omega-OH-Em$ ) |

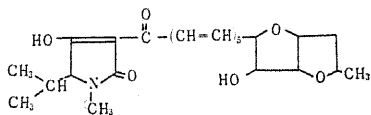
変形-Bisanthraquinone 系



- |   |                          |                                    |
|---|--------------------------|------------------------------------|
| (-) Luteoskyrin (Deoxy-)<br>(4a-Oxyluteoskyrin) | (-) Rubroskyrin (Deoxy-) | (+) Rugulosin<br>(4a-Oxyrugulosin) |
|---|--------------------------|------------------------------------|



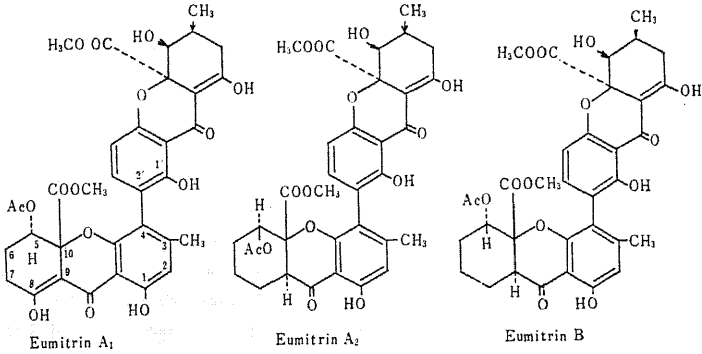
(-) Flavoskyrin



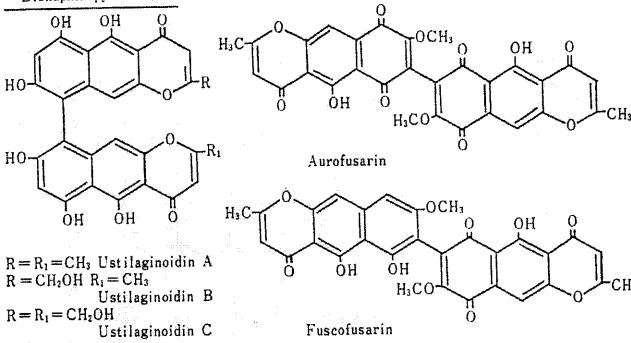
Erythroskyrin

Fig 2

变形-Bisxanthone-系



Bisnaphthopyrone-系



变形-Bisphenalenone系

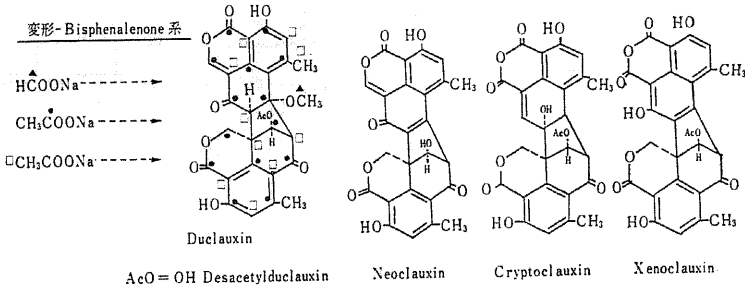


Fig 3

Biosynthesis

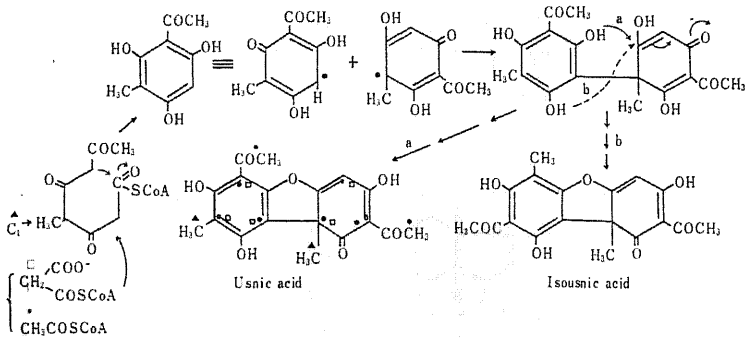
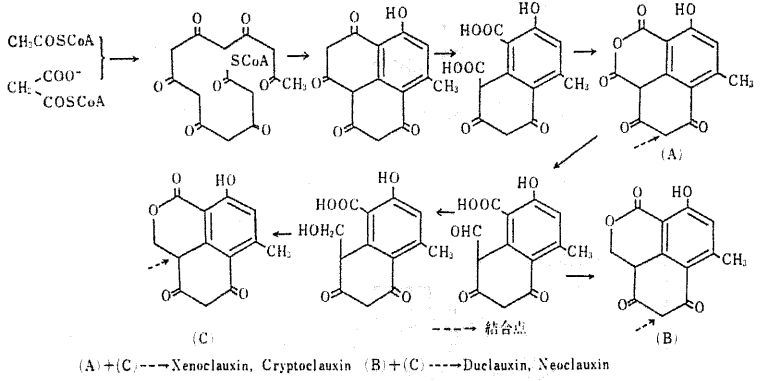
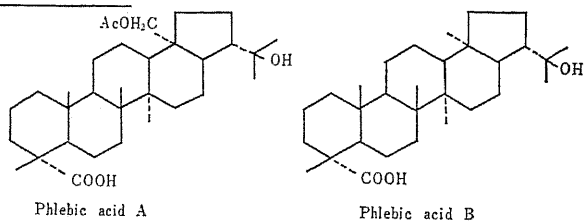
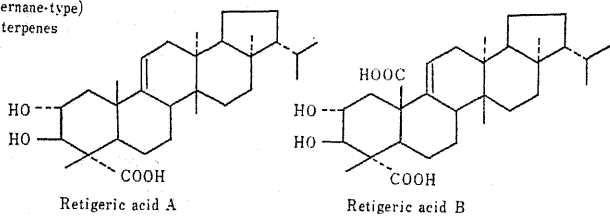


Fig 4

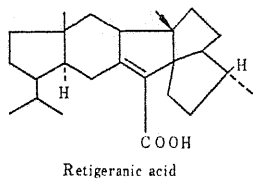
Hopane type triterpenes



Migrated hopane-type  
(Fernane-type)  
triterpenes



Sesterpene



一、主要な論文及び著書目録

- (I) 菌類及び地衣類の代謝産物の研究
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