

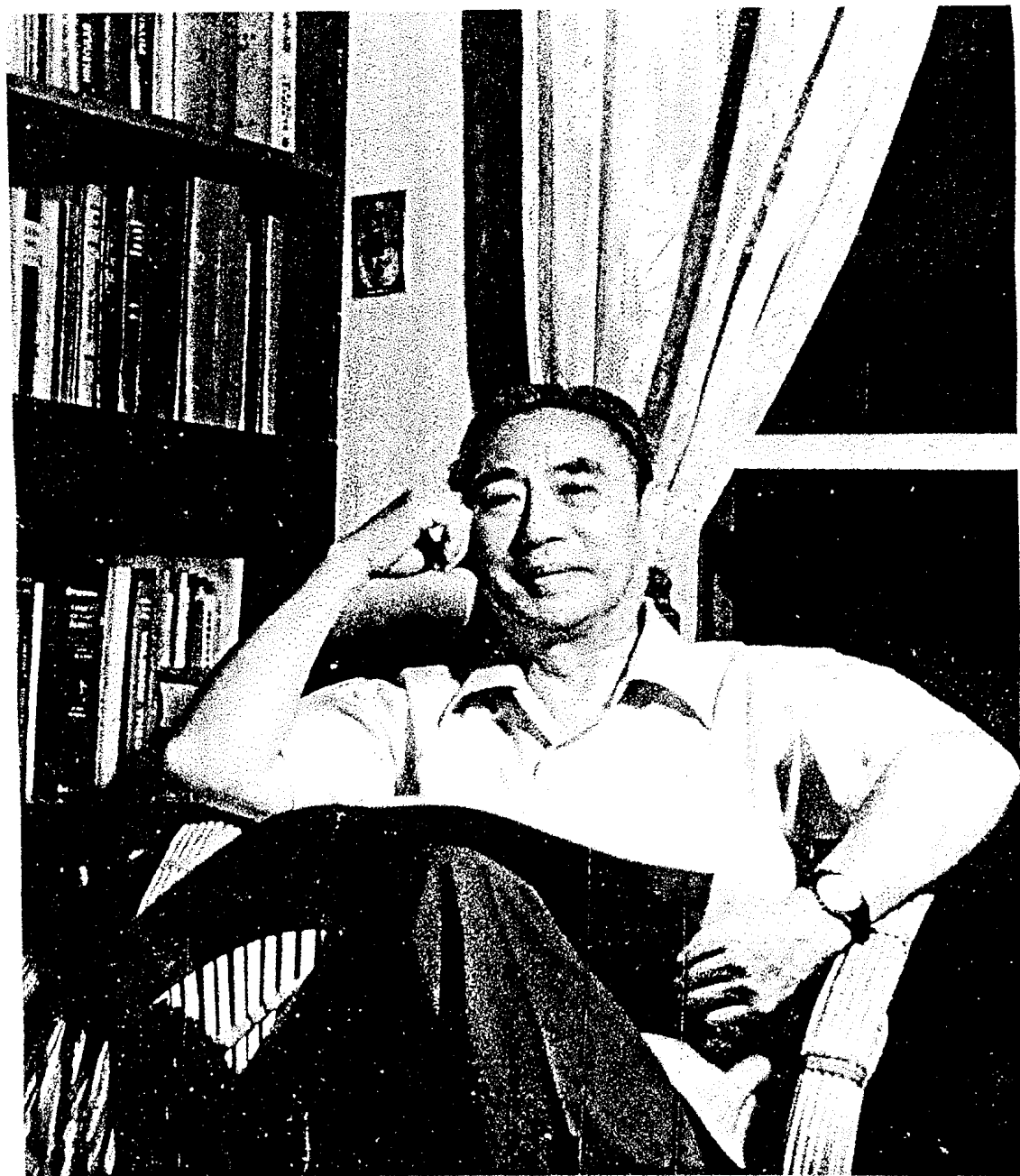
黄耀曾教授学术论文集

——庆祝黄耀曾教授八十寿辰

(一)

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FOREWORD

Professor Yao-Zeng Huang was born in 1912 in Nantong, Jiangsu, China, and received his B.S. in 1934 from the National Central University in Nanjing. He was appointed professor at the Shanghai Institute of Organic Chemistry in 1951, deputy director of the same institute in 1960, and was elected to membership in the Chinese Academy of Sciences and to the deputy directorship of Chemistry Division, the Chinese Academy of Sciences in 1980.

Before 1949, he took part in the early attempt of total syntheses of steroid under the direction of distinguished chemist, late Professor Chang-Kong Chuang. After 1949, he became a group leader directed to the chemistry of tetracycline and then a department chairman engaged in the government projects of national defense. He has been dealing with the development of new methods of organic syntheses via organometallics, especially organoarsenic, organoantimony and organotellurium compounds.

Professor Huang and his coworkers found a facile olefination method for the synthesis of unsaturated aldehydes, ketones, amides and related natural products directly via arsonium salts in the presence of potassium carbonate at room temperature under phase transfer conditions. Of particular interest is the catalytic Wittig-type reaction: the tri-n-butylarsine-catalyzed olefination in the presence of triphenyl phosphite (J. Org. Chem. 54, 2027(1989) and see also CHEMTRACTS—Organic Chemistry 2, 300(1989)). Its simplicity, moderate reaction conditions, high E stereoselectivity and good yields make it a practical alternative for large scale synthesis (Y.Z. Huang et al., Heteroatom Chemistry, Block E. Ed.; VCH Publishers: New York, 1990; pp189-206). As for research on organoantimony compounds in organic synthesis, Huang et al. found that in contrast to triphenylstibine, trialkylstibine react with α -halocarboxylic derivatives or α -haloketones readily to form quaternary stibonium salts, the reaction of which can be classified into three categories: (1) Reactions of the quaternary stibonium salts with substrates without the use of added base. (2) Reactions of the quaternary stibonium salts on treatment with strong nucleophile afforded pentaorganylstiborane (λ^5 -stibanes), which react with aldehydes to give, after hydrolysis, secondary alcohols. (3) Reactions of quaternary stibonium salts with less nucleophilic strong bases such as LDA or potassium tert-butoxide afford stibonium ylides, which react with carbonyl compounds to produce olefins or epoxides (Y.Z. Huang, Acc. Chem. Res., 1992, 25, pp. 182-187). Diphenyltelluronium methylide, a first non-stabilized telluronium ylide, react with carbonyl compounds to afford substituted oxiranes; under phase transfer conditions, allyldiisobutyltelluronium bromide reacts directly with aldehydes at room temperature to give α,β -unsaturated epoxides; in the presence of cesium carbonate, under phase transfer conditions, a first example of Wittig-type epoxidation has achieved.

In 1980 and 1982, Professor Huang organized and served as Chairman of the First and the Second China-Japan-USA Symposium on Organometallic Chemistry held in Beijing and in Shanghai respectively, and in 1984 as Co-chairman of the Third China-Japan-USA Symposium on Organometallic Chemistry held in Santa Cruz.

He is the founder of organic microanalysis, pioneer of organometallic chemistry as well as organofluorine chemistry in China. He received numerous honors which include the Chinese Academy Award, the National Science Conference Award, the National Award of Progress of Science and Technology and "Devoted oneself to National Defense" Medal. He is the member of advisory editorial board of three international journals, Synthesis and Reactivity of Inorganic and Metal-organic Chemistry, Heteroatom Chemistry, and the Journal of Asian Chemistry. He has served as Visiting Professor to the University of Notre Dame and the Chinese University of Hongkong. He has published about 210 scientific papers in domestic and foreign journals. Out of that, 142 papers are selected in this collection.

The Editor

October 15, 1992

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V. MISCELLANEOUS

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VI. APPENDICES

824

二十五年来天然有机化合物的合成的成就

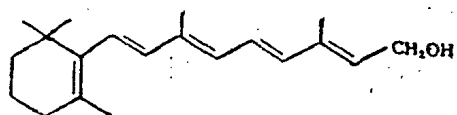
黄耀曾

(中国科学院有机化学研究所)

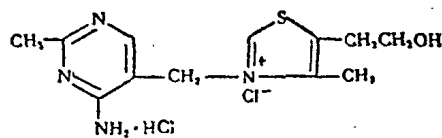
自从Kekule提出了碳是四价的假设(1857)以来,到现在恰好是一百年。他和他同时代的Byrnesopos奠定了有机化学结构理论的基础,从而使得有机化学有了很大的发展。一百年以前除掉Wöhler(1828)的划时代贡献,合成尿素,Kolbe(1845)合成醋酸以外,天然有机化合物合成的工作很少。由于结构学说的逐渐确立,有机合成便大放异彩。Caro, Graebe, Liebermann(1868)合成了茜草素(alizarin), Landenburg(1886)合成了毒芹碱(coniine), Behrend和Roosen(1886)合成了尿酸, Heumann(1890)合成了靛蓝(indigo), Emil Fischer(1890)合成了几种糖。接着是Fischer(1901)多肽的合成, A. Pictet(1904)烟碱(nicotine)的合成, Komppa(1909)樟脑的合成,都是些极其光辉的成就。这是十九世纪以及二十世纪初叶的事。

二

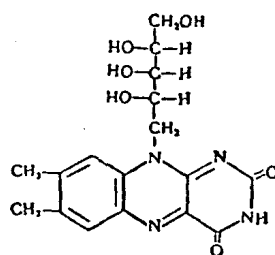
最近二十五年来天然有机化合物的合成有了飞跃的进展。维生素方面: A (I), B₁ (II), B₂ (III), B₆ (IV), C (V), D (VI), E (VII), K (VIII), 泛酸(pantothenic acid) (IX), 生物素(biotin) (X) 和叶酸(folic acid) (XI) 都一一被合成了。其中几种,例如维生素B₁(Williams, 1936), B₆(Kuhn, Merck 实验室, 1938—1939), 生物素(du Vigneaud, Merck 实验室, 1943)的合成,几乎是和结构的阐明同时完成的;而维生素K(Fieser, 1939)则和一般的传统不同,是用合成的方法来阐明结构的。维生素A的合成(Isler, 1947)距离结构的阐明(Karrer, 1931)不过十六年,维生素D的提纯在1931年,它的半合成去年由Inhoffen^[1]实现了。



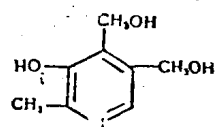
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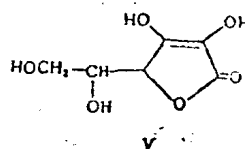
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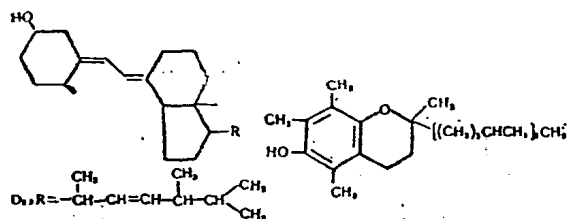
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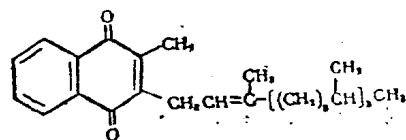
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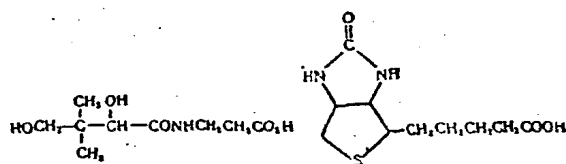


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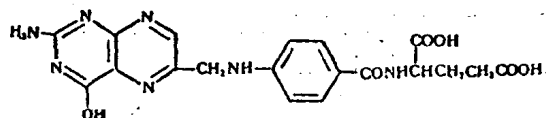
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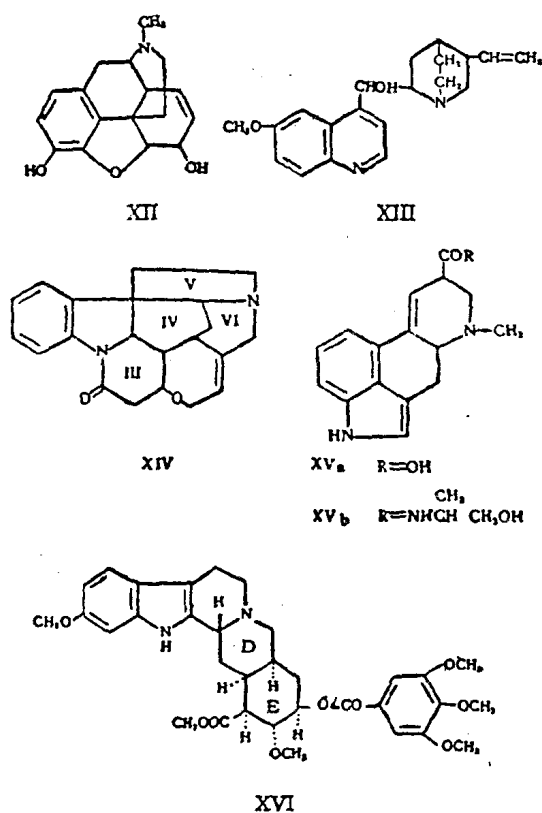
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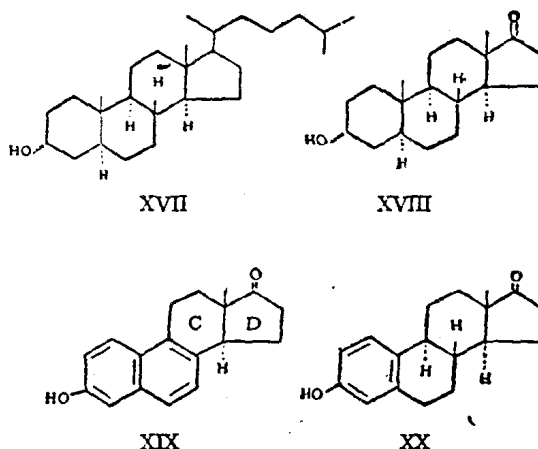
XI

植物碱中最早发现和提纯的有吗啡 (XII)、奎宁 (XIII)、番木碱 (XIV) 等。这些一向被认为是极难合成的化合物, 都在最近合成成功。吗啡的全合成是 Gates^[2](1952) 和 Ginsburg^[3](1954) 的成就, 距离它的提纯差不多晚了一百五十年。奎宁和番木碱^[4]的全合成都是 Woodward 的贡献, 这位震惊化学界的杰出有机化学家并在最近光辉地完成了其它两种重要植物碱的全合成——麦角植物碱 (ergot alkaloid)^[5]: 麦角酸 (lysergic acid) (XVa), 麦角新碱 (ergonovine) (XVb), 以及蛇胆石 (reserpine)^[6] (XVI)。

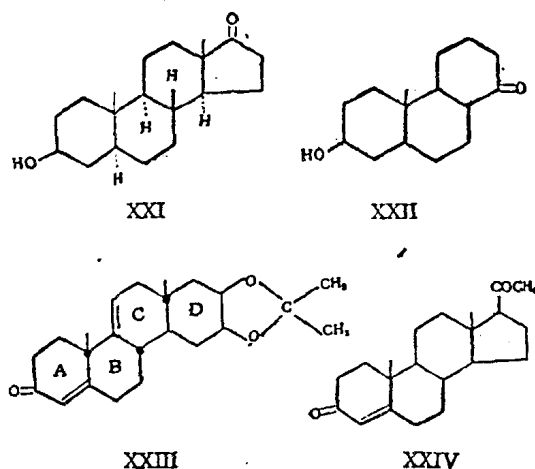


甾体化合物方面, 自从 Rosenheim, King, Wieland (1932) 在二十五年前提出了新的公式以后, 它们的部分合成和全合成一直是各国有机化学家奋斗的目标。我国庄长恭也曾领了一小队工作者从事于此。部分合成首先获得成功的是 Ruzicka (1934), 他用 epidihydrocholesterol (XVII) 氧化, 得到 androsterone (XVIII), 虽然当时对于这样反应应该称为合成还是降解曾经引起了有机化学界热烈的争论。Bachmann (1939) 的 equilenin^[7] (XIX) 的合成是甾体化合物中全合成首先获得成就的工作。接着, Johnson (1945) 用完全不同路线来构造 equilenin 的 D 环也获得成功。Estrone (XX) 的全合成经 Miescher^[8] (1947—1949), Johnson 等^[9]

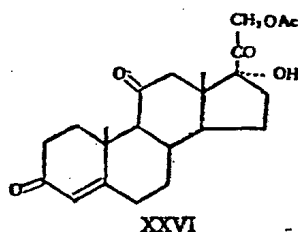
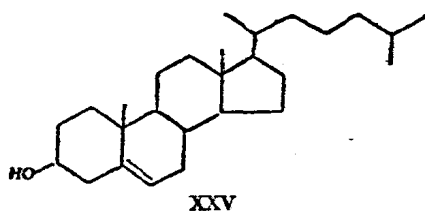
(1952) 分别研究而底于成。值得指出, 他们除 estrone 本身外还获得其它七种外消旋异构体, 得到了所有理论上可以存在的异构体。



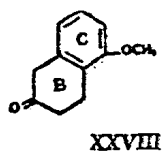
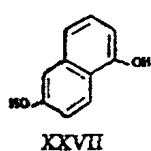
非芳香族的甾体化合物, 由于它们含有许多不对称碳原子, 立体异构体太多, 一向被认为是极难合成的。1952 年两处同时宣布合成成功, 一处是 Robinson^[10] 的实验室, 一是 Woodward^[11] 的实验室。事实上 Robinson 合成 epiandrosterone (XXI) 的中间体 (XXII) 早在 1946 年已经获得, 经过了差不多五年才得到最后成功, 可见工作是极其艰巨的。Woodward 的甾体化合物合成的特点是从中间体 (XXIII) 出发, 可以制备各种非芳香族的甾体化合物, 例如 androsterone (XVIII), 妊娠激素 (progesterone) (XXIV), 胆固醇 (cholesterol) (XXV), cortisone (XXVI), 几乎把非芳香族甾体化合物一网打尽。这一合成路线设计的特点是在 A 环和 C 环上巧妙地安下两个双键, D 环则是六员环, 使得 C, D 环在合成过程中稳定地保持反式稠合。最后将 D 环氧化成双醛, 环化后成为 C-17 位置上含有一



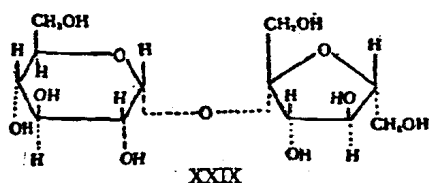
个甲醛基的甾体骨架。C-17 的甲醛基则是合成边链的出发点, C 环上的双键则是合成 C-11 酮基的基础。



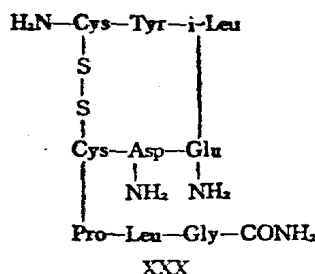
Sarett 最初用胆酸改造合成 cortisone, 后来又报告了全合成的方法^[12]。最近 Johnson^[13]也报告了非芳香族甾体化合物的全合成。值得指出, Robinson 方法的起始原料是 1,6-萘二酚 (XXVII), 从而制备了化合物 (XXVIII), 作为甾体 B, C 环的基础。Johnson 的方法用同样的原料, 把它作为 C, D 环的基础。足见有机合成设计的运思是各有巧妙不同的。



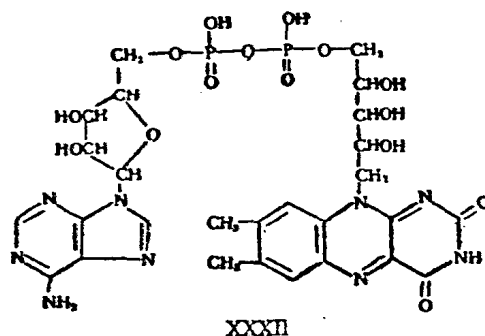
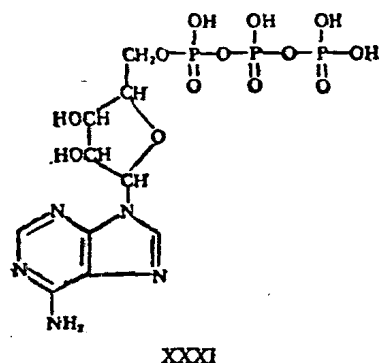
碳水化合物方面: 蔗糖 (XXIX) 的合成一直被人们所注意, 达数十年之久, 1953 年为 Lemieux^[14] 实现了。虽然 Hassid (1944) 曾经用葡萄糖-1-磷酸酯和果糖经过酶的作用合成了蔗糖, 但用纯粹的化学方法来合成, 过去一直没有人达到目的。



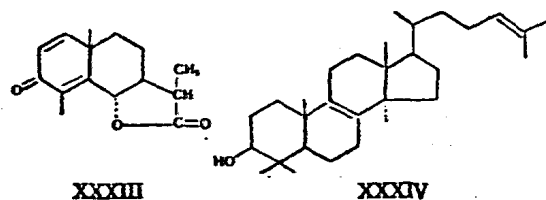
催产素 (oxytocin) (XXX) 的合成是近年来一件大事。这次 de Vigneaud^[15] (1954) 光辉的成就鼓舞了多肽合成的信心, 无疑会成为今后有机化学工作的重点。将来较大分子的蛋白质例如胰岛素的合成不是不可能实现的。



核武酸: adenosine triphosphate (XXXI) 及 flavine-adenine dinucleotide (XXXII) 的合成, 是 Todd 等^[16] 的辉煌贡献。

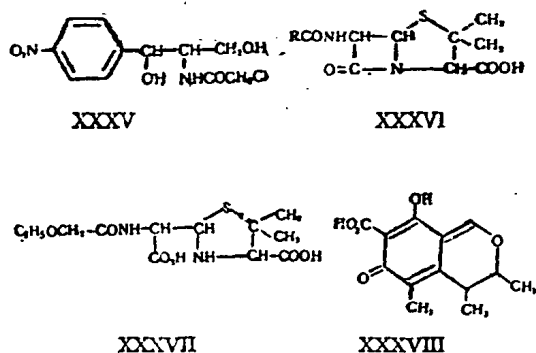


萜类化合物山道年 (XXXIII) 的合成, 虽然远在十几年前有人宣布合成成功, 并且宣称不从任何不对称合成 (asymmetric synthesis), 一下子就得到旋光活性的产物, 旋光度居然和天然山道年相同; 但是显而易见, 他的工作是不可能重复的, 就是他本人也断然不会重复的。留下的只是谈话柄而已! 日本学者 Abe^[17] 山道年的合成是近年来萜类化合物中重要贡献。他不但合成了天然山道年, 并且也获得了所有理论上可能存在的一切立体异构体。四环萜类



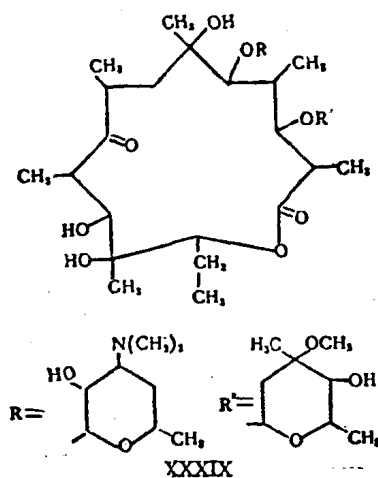
lanosterol (XXXIV) 的合成也由 Woodward 和 Barton^[18] 合作实现了。

重要抗生素的合成有氯霉素 (XXXV)，它已完全代替了生物合成，大规模地生产^[19]。我国高怡生、邢其毅在氯霉素合成方面也有贡献。青霉素 G (XX XVI, R=C₆H₅CH₂) 的合成，虽过去有人宣布成功，不过产率仅万分之一。最近 Sheehan^[20] 利用 N, N'-dicyclo-hexylcarbodiimide 为缩合剂，在水溶液中将 (XXXVII) 缩合，合成了青霉素 V (XXXVI, R=C₆H₅OCH₂)，产率 10—12%。橘霉素 (XXXVIII) 也已合成，我国汪猷也有贡献。



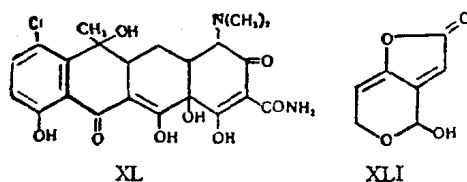
三

科学研究是不能一蹴而就的。搞清化合物的结构是合成的基础。有机化学家探索番木甙碱、吗啡结构的秘密的工作，实际上在有机化学成为一种学科以来的全部历史中展开着。人们对甾体化合物的结构的研究也贯穿了三十多年的有机化学史。抗生素的研究无论在微生物学方面或有机化学方面，近二十年发展很快。它们结构的阐明往往在短期内突破。青霉素的结构经过了英美两国有有机化学家 (Robinson, Chain, Folker, Woodward, du Vigneaud 等) 集体研



究，终于成。结构古怪陆离的紅霉素 (erythromycin^[21]) (XXXIX)、金霉素 (chlorotetracyclin) (XL) 也是在短期内予以肯定的。

当有机化学家们合成一种天然有机化合物时，首先要感谢的是这种化合物结构的奠定者。Wieland, Wieland 在甾体化合物结构研究中光辉的贡献，Leuchs 在番木甙碱结构研究中辛勤累积的巨大资源，Robinson 天才地描繪嗎啡结构的图形都是化学家做合成时设计的张本。虽然有时一些结构上的细节还没有搞清 (例如一两处立体化学上的问题)，在合成时反可明朗化。Lanosterol (XXXIV) C-14 的甲基在 α 位就是用合成方法才证明的^[18]。抗生素 patulin^[22] (XLI) 的结构是用合成来决定的。

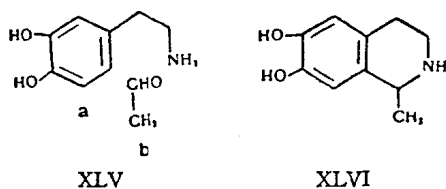
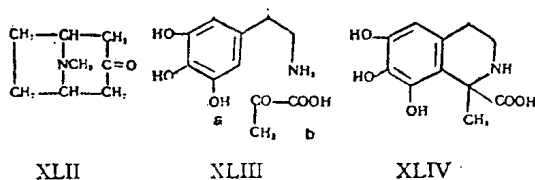


其次，必须指出，有机合成是不能以成败论英雄的。Robinson 甾体化合物的合成，一系列的文章，发表到第 50 篇时，并没有合成成功任何一种天然甾体化合物，而 Bachmann, Johnson, Miescher 合成 equilenin, estrone 的工作，相继发表了。然而谁能否认 Robinson 合成甾体的工作实光辉地驾乎他人之上呢？Robinson 不急于求成，精心地筹划各种巧妙合成路线，发展了合成的方法，丰富了有机化学内容，无论反应成功和失败，都可作其他有机化学家做合成时的借鉴。

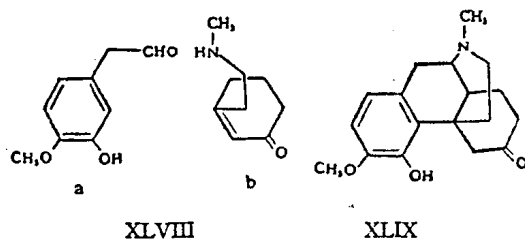
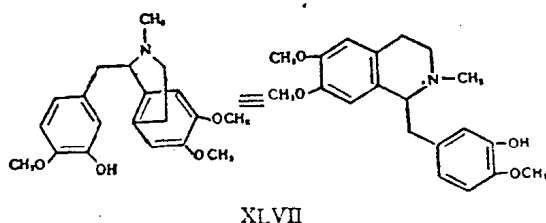
吗啡合成的先驱者如 Grewe, 番木甙碱合成的先驱者如 Leuchs 的工作，何尝不是 Gates 以及 Ginsburg 合成吗啡，Woodward 合成番木甙碱可贵的参考资料呢？此外，那怕是极其微薄的合成方面的贡献，看来虽和有机化学家着手进行的合成工作无关，也是可贵的。

四

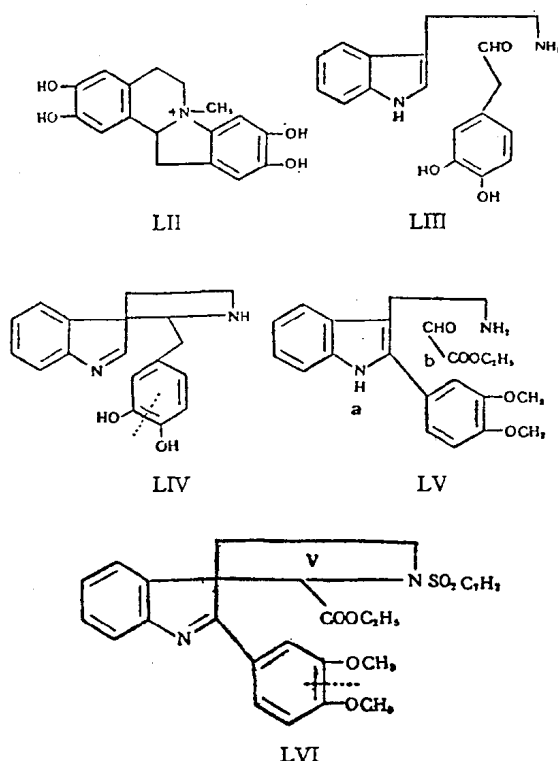
生源学说对天然有机化合物的合成是不是起了指导作用呢？Robinson (1917) 的 tropinone (XLII) 的合成，戏剧性地说明了这一问题。丁二醛、甲胺、丙酮二羧酸混合物的水溶液放置片刻得到 tropinone 已是众所周知的事实了。其它两个例子在所谓“生理条件”的酸度与温度下起了下列的变化 (XLIII_{a,b}→XLIV), (XLV_{a,b}→XLVI)。后者 (XLVI) (norsalsolin) 的收获率达到 83%。



Robinson 指出了嗎啡 (XII) 与苄基异喹啉植物碱如 laudanone (XLVII) 的相似关系, 因而 Woodward 制备了 XLVIII_a 与 XLVIII_b 两个组分, 希望经过变化生成 dihydrothebaine (XLIX), 可是事实上得到的只是 (L)。Robinson 企图从苄基异喹啉植物碱 (LI) 转变成吗啡类化合物的氧化过程中, 得到的只是一种季胺盐 (LII), 有兴趣的是在 Robinson^[23] 工作发表后的二十年, 这种季胺盐的三甲醚居然在自然界找到了^[24]。



番木碱 (XIV) 第 V 环的生源, Woodward^[4] 明辨了是由于一种醛在色胺 (tryptamine) 吲哚核的 β 位缩合而形成的 (LIII→LIV)。他利用 ethyl glyoxalate (LV_b) 和色胺衍生物 (LV_a) 缩合, 构成番木碱的第 V 环得 (LVI)。



另一种重要的推测, 番木碱的生源包括碳环的裂开 (如在式 LIV 中虚线所示), Woodward 在色胺组分巧妙地预先安上邻位二甲氧苯基 (LV_a), 在碳环裂开后 (式 LVI 虚线所示) 可作为构造 III, IV, VI 环的基础。

上述的许多例子是应用生源学说来指导合成的。另一方面, 完全不管生源学说, 合成获得成功的, 文献中也不乏先例, Gates 和 Ginsburg 吗啡的合成是这类例子。

五

科学是不能孤立发展的。近二十五年来天然有机化合物合成的进展和新反应的发现、方法的改进分不开的。双烯合成 (Diels, Alder, 1928) 广泛的应用是近二十五年间的事。Reserpine (XVI) 的合成第一步骤是应用的双烯合成 (LVII_{a,b}→LVIII), 生成物 (LVIII) 经过一系列的反应得到 LIX, 然后再与取代色胺 (LX) 缩合制得主要的中间物 (LXI)。

