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A REVIEW ON RECENT DEVELOPMENTS IN PALLADIUM CATALYZED SUZUKI-MIYAURA CROSS-COUPLING REACTIONS

Pharmaceutical Science

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ABSTRACT

Suzuki-Miyaura reaction has been an approach towards use of green chemistry for the synthesis of novel compounds via cross-coupling reaction between Substituted aryl halides and substituted phenyl boronic acids. The reaction is usually conducted in the palladium based catalyst, a transition metal that forms complex with various ligands, along with aryl halide and substituted phenyl of boronic acid, thereby forming a new C-C bond between aryl group in aryl halide and substituted phenyl. The palladium catalyst can be reused, until it is being converted to palladium black. In the recent years, efforts have been made to increase the catalytic life of palladium by converting it to either nanoparticles or binding with some polymer which retards its conversion to palladium black and hence can be recycled, after washing with a suitable solvent.

KEYWORDS

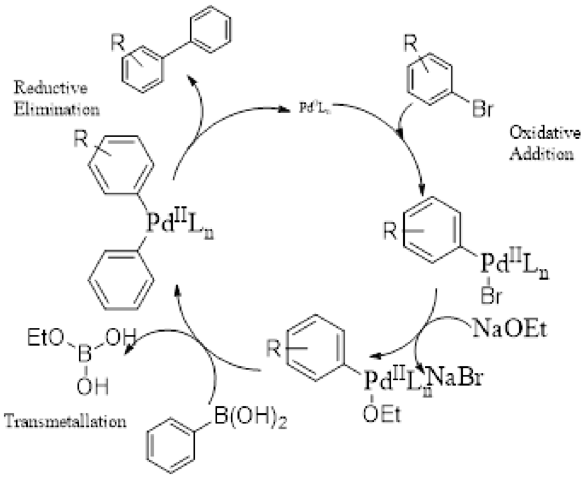
Suzuki-Miyaura Reaction, Palladium, Aryl Halide, Phenyl Boronic Acid

INTRODUCTION

The most important and vital step in chemical reactions is the formation of carbon-carbon bond be it the formation of an enzyme or protein in body, a chemical moiety for medicinal, agricultural, domestic use or development of novel organic materials[1,2]. Since past 40 years, various reaction methodologies based on metal complexes have been developed for introducing carbon-carbon bond formation. In pharmaceutical chemistry, various cross coupling reactions namely, Kumanda-Corriu, Negishi, Suzuki-Miyaura and Stille have been used widely to obtain new pharmaceutical and fluorophores, but since discovered in 1979, Suzuki-Miyaura reaction or Suzuki coupling has been utilized as one of the major coupling tools. The reaction involves the palladium catalyzed coupling of an organic halide, alkenes, alkynes or organometals with an organoboron in alkaline medium (scheme-1)[3,4]. The reaction is usually carried out in three steps with temperature maintained to 60-80°C[5]:

a) Oxidation of Pd (0) to Pd (II) by organic halide
b) Transmetallation
c) *trans-cis* rearrangement followed by reduction thereby regenerating the catalyst.

(i) Example of Suzuki-Miyaura reaction



(ii) Mechanism of Suzuki-Miyaura reaction
Scheme-1

Suzuki coupling offers various advantages over other coupling methods, which renders it a coupling method of choice[6,7]:

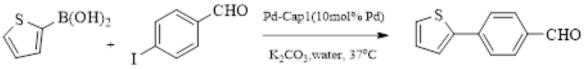
(i) water stability
(ii) mild reaction conditions
(iii) easily available reactants
(iv) favoured in aqueous and heterogeneous reaction mixtures
(v) can be used against a wide range of functional groups
(vi) steric hinderance is insignificant
(vii) reactions are region and stereoselective
(viii) quantity of catalyst to be used is small
(ix) can be used in one pot synthesis
(x) inorganic boron developed at the end of reaction can be separated easily

Suzuki-Miyaura cross coupling reaction can be carried out in aqueous, organic or biphasic (aqueous/organic) solvent system. But owing to the toxicity of organic solvants, there has been a search for a better alternative as solvent. Water, being non-toxic, cheap, abundant, non-inflammable and its property to solublize a wide range of inorganic salts, makes it a solvent of choice. The problem related to containinated water disposal, can however, be minimized by using cetain polymeric support for catalyst, thereby increasing their life. Use of catalysts in nanoparticle form, further increases their efficiency. In addition to aqueous and organic solvents, aqueous extracts, oligomers, ionic liquids, deep eutectic solvents, supercritical carbon dioxide and bio-mass derived solvents also provides a good and safe solvent medium[8,9].

PALLADIUM-CATALYZED SUZUKI-MIYAURA REACTIONS

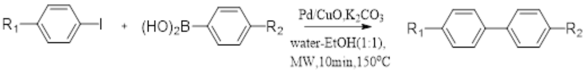
Palladium owing to its complex forming tendency by activation of organic compounds has been utilized as the vital tool for reaction catalysis. Furthur, its property to catalyze a reaction in aerobic conditions, is exploited in Suzuki-miyaura cross coupling reaction using it as catalytic system in nanoparticle form or as complex with a ligand[10]. Various metals other than palladium, have been employed as catalysts for Suzuki coupling reactions including nickel, iron, gold, copper and cobalt as nanoparticles along with a combination of gold-palladium, silver-palladium and copper-palladium nanoparticle. There have been efforts to develop a palladium based catalytic system with high efficiency in aerobic conditions and is recyclable. In this approach, various catalytic systems with palladium developed, to be used in Suzuki-miyaura cross coupling reaction have been reviewed.

Destito et al. devised hollow nanoreactors charged with palladium, by fabricating nanoshells of mesoporous silica and coating inner layer with palladium nanoparticles. The nanoreactors allowed palladium catalysed Suzuki coupling reaction to undergo in aqueous solvents at physiological temperature, which otherwise gives no reaction owing to deactivation of palladium complexes. 2-Thiophenyl boronic acid was coupled with *p*-iodo benzaldehyde, using hollow Pd-nanoreactors and aqueous Potassium carbonate at 37°C. A 55% yield of 4-(thiophen-2-yl) benzaldehyde was obtained after 3hrs and 78% when reaction was continued for 24hrs as same temperature (Scheme-2)[11].



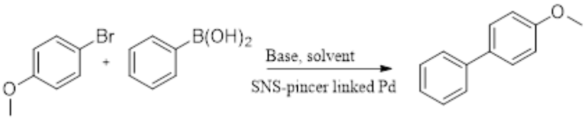
Scheme-2

Elazab et al. described copper oxide supported palladium nanoparticles, for microwave-assisted Suzuki cross-coupling reaction. The reaction involved dissolution of aryl halide in water-ethanol (1:1) mixture, followed by addition of aryl boronic acid, potassium carbonate and Pd/CuO, and irradiated with microwaves at 80°, 120°, 150°C for 10 min when the coupled product is obtained in 100% yield. After washing for five times with ethanol, the catalyst can be reused (Scheme-3)[12].



Scheme-3

Fiebor et al. reported the use of water soluble SNS-pincer-palladium complex for Suzuki coupling of phenylboronic acid with aryl halides using K_3PO_4 as the basic media, with 92% yield of the final product. The catalytic system was i.e., SNS-pincer-palladium complex was also reported to be reusable for three conseceutive reaction cycles, without activity loss(scheme-4)[13].

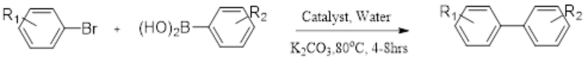


Scheme-4

Base: K_3PO_4, Pyridine, Triethyl amine, Potassium Hydroxide, Potassium carbonate or Cesium carbonate

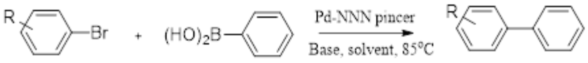
Solvent: Water, DMF, Toluene or water-mercury mixture.

Li et al. reported the use of $PdCl_2$ supported over fullerene, as an efficient coupling agent providing 99% yield of the final coupled product at room temperature. The catalyst was formed by cross-linking fullerene nano-particles with $PdCl_2$, making it highly water soluble. The cross-coupling reaction was carried in the presence of potassium carbonate as base (Scheme-5)[14].



Scheme-5

Yadav et al. used NNN-pincer palladium complex based on bis-(pyrrolyl)pyridine as catalytic system for coupling of aryl bromides in different solvent systems. Maximum yield was obtained with ethanol-water (3:2) mixture than pure ethanol or water, and K_2CO_3 as base. The reaction was found to be regioselective, even with the *p*-substitution of chlorine atom on aryl bromide (Scheme-6)[15].

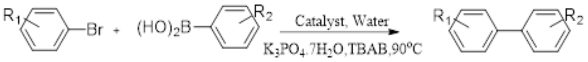


Scheme-6

Base: Potassium carbonate, Potassium phosphate, Potassium hydroxide

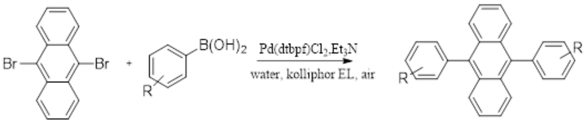
Solvent: Water, Toluene, Methyl cyanide, Ethanol, Ethanol-water, THF-water, Dioxane-water, DMF-water

Zhou et al. reported the use of mono-6-($_L$-aminopropanol)-deoxy-β-cyclo-dextrin based palladium catalyst in order to increase the catalytic efficiency in Suzuki-miyaura cross coupling reaction in water as solvent. The reaction involved cross-coupling of aryl bromides and aryl boronic acids using $PdCl_2$-cyclo-dextrin complex in aqueous media. A high yield of biaryl derivatives 80-100% was obtained, when reaction mixture heated for 4hrs at 90°C in the presence of $K_3PO_4.7H_2O$ and tetra-*n*-butylammonium bromide (TBAB). The catalyst was found to be recyclable for six reaction cycles, when extracted with diethyl ether (Scheme-7)[16].



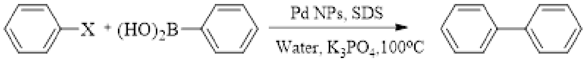
Scheme-7

Beverina et al. described aerobic medium composed of micelles for Suzuki cross coupling based synthesis of diketopyrrolopyrroles, diarylanthracenes, isoindigos, diarylbenzothiazoles and perylenediimides. Reaction involved coupling of aryl and heteroaryl bromides with aryl boronic acids and esters, providing a high yield even when the reaction was conducted in oxygenated environment with deionised water as solvent (Scheme-8)[17].



Scheme-8

Khan et al. prepared palladium nanoparticles using the aqueous solution of extract from root of *Salvadora persica* L. and were utilized in Suzuki Miyaura cross-coupling reaction as catalyst under aqueous medium. The root extract contains polyphenolic phytomolecules showing reduction of Pd nanoparticles, activates its surface and also a stabilizer in different solvent systems. Aqueous solution of palladium nanoparticles was used for Suzuki coupling of phenyl halides and phenylboronic acid yielding biphenyl system. Reaction was carried out at 100°C in the presence of potassium phosphate (Scheme-9). Catalyst developed was reusable but showed a considerable decline in activity after three consecutive cycles[18].

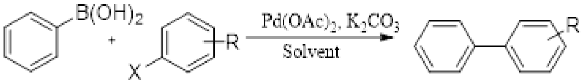


Scheme-9

Pitchumani et al. reported stabilization of ionic form of Pd (II) complex, by means of β-cyclodextrinmodified using water soluble pyridinium. The stabilized palladium complex was used to catalyze Suzuki cross coupling reaction of aryl halides with phenyl boronic acid and provided 72-95% final yield of the coupled product. The reaction involved heating of reacting species at 80°C for 30min-2hrs in the presence of potassium phosphate as base. The catalyst developed was found to be highly water soluble and can be recycled for more than six times without loss of catalytic activity (Scheme-10)[19].

Scheme-10

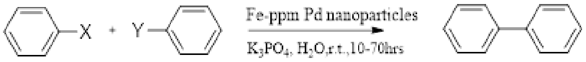
Hoffmann et al. carried out ligand-free and ligand-assisted Suzuki coupling of phenylboronic acid and aryl halids in water, dioxane, dioxane-water (1:1), ethanol-water (1:1), using K_2CO_3 as base. In ligand free conditions, ethanol-water mixture and water provided high yield of the coupled product, with dioxane yielding least. Dioxane was, however, when replaced with dioxane-water mixture, a considerable increase in final yield was reported (scheme-11)[20].



Scheme-11

Solvent-Water, Ethanol, Dioxane, Ethanol-water (1:1) mixture, Dioxane-water (1:1) mixture

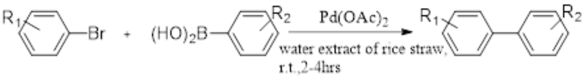
Lipshutz et al. demonstrated the use of ferric chloride ($FeCl_3$) directly in cross-coupling reaction, since it already contains palladium in ppm. The reaction, however, made use of 2-dicyclohexylphosphino-2,6-dimethoxybiphenyl (SPhos) ligand. Ferric chloride based catalyst was found to be highly efficient in coupling reaction of aryl halide with aryl or alkenyl boron derivatives, as provided 95% final yield. The catalyst was prepared by SPhos and palladium acetate catalyzed reduction of ferric chloride with MeMgCl. When however, use of ferric chloride doped with metals such as nickel chloride, manganese chloride, cobalt chloride, cupric acetate or cuprous bromide, resulted in reduction of the yield to 38% (Scheme-12)[21].



Scheme-12

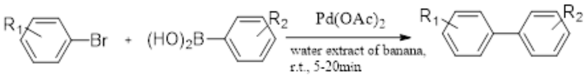
X: I, Br, Cl; Y: $B(OH)_2$, BMIDA, Bpin, BF_3K

Saikia et al. prepared aqueous extract of rice straw ash to be used as catalyst along with palladium acetate in Suzuki-miyaura reaction. The coupling of aryl bromide and aryl boronic acid was found to proceed smoothly at room temperature, in the absence of alkali, ligand or promoter, providing about 90% final yield. The catalytic medium was found to be reusable, with a reduction in activity (Scheme-13)[22].



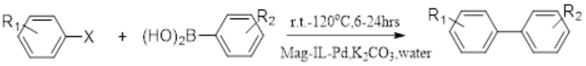
Scheme-13

Saikia et al. reported the preparation of water extract of banana peels for Suzuki-cross-coupling in ligand free conditions. The reaction was catalysed by palladium acetate in the absence of any ligand or base and provided with 99% yield in about 90min. A reduction in activity was noted, when catalyst was recycled for consecutive reaction (Scheme-14)[23].



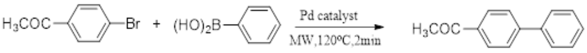
Scheme-14

Karimi et al. used water dispersible form of palladium in Suzuki-cross coupling reaction of aryl halide with aryl boronic acid. Catalytic form of palladium was prepared by linking with Fe_3O_4 associated with SiO_2, further bonded with hydrophilic triethylene glycol-imidazolium. The coupling reaction carried in aqueous medium by heating the reacting species at 120°C for 6-24hrs with potassium carbonate as alkali until completion. The catalytic complex prepared can be reused for about 10 reaction cycles without any loss of catalytic activity (Scheme-15)[24].



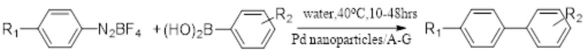
Scheme-15

Shen et al. reported synthesis of pyridine-pyrazole N-N ligand bonded with palladium (II), and acts as a water soluble catalyst for Suzuki reaction of aryl halide and aryl boronic acids. The reaction was conducted in a sealed glass vessel by irradiating with microwaves in scientific microwave in the presence of a base and ethanol-water mixture as solvent system. 99% conversion was achieved with KOH as base (Scheme-16)[25].



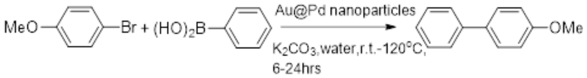
Scheme-16

Cacchi et al. catalyzed coupling reaction between arene diazonium salts and potassium aryl trifluoroborates in air using palladium nanoparticles stabilized with alginate/gallan. A 90% yield was obtained, when reaction mixture was refluxed under phosphine free conditions and in the presence of aqueous solution of a strong base for 10-48hrs. A 0% coupled product was however noted, when reaction was carried in methanol, ethanol, cyanomethane or DMF. The catalyst developed can be used for eight reaction cycles consecutively (Scheme-17)[26].



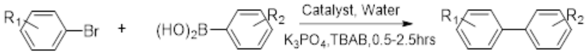
Scheme-17

Jutang et al. described use of gold-palladium (Au-Pd) nanoparticles for Suzuki-miyaura reaction in aqueous media. The nanoparticles catalysed the coupling of p-methoxyphenyl bromide with phenyl boronic acid at room temperature in the presence of potassium carbonate and provided with the final derivative in roughly 4hrs (Scheme-18)[27].



Scheme-18

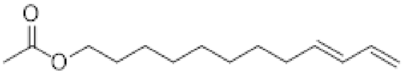
Jin et al. reported the use of Palladium acetate immobilized using MFI zeolite support for Suzuki-miyaura cross coupling between aryl bromide with aryl boronic acid in aqueous media, the substrates were refluxed for 2hrs using potassium phosphate as base (Scheme-19)[29].



Scheme-19

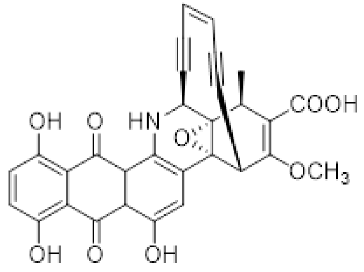
NATURAL PRODUCTS DEVELOPED USING SUZUKI-MIYAURA CROSS COUPLING REACTION

Suzuki-Miyaura cross-coupling reaction finds a major application in the synthesis of natural as well as synthetic drugs. Till date over 500 natural compounds have been synthesized via cross-coupling reaction[62]. In the year 1975, Nesbitt et al. isolated a pheromone from an insect *Diparopsis castanea*[29], It was the first natural compound synthesized using Suzuki-miyaura reaction by Rossi et al in 1981[30].



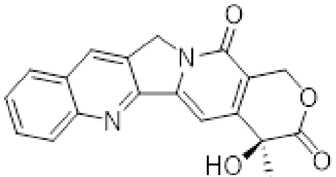
Insect pheromone 121

Later, in the year 1995, Myers[31]. and Shair et al[32]. individually reported the synthesis of Dynemicin A, an antitumor agent isolated from soil in Gujarat in India and is indigenous to *Micromonospora chersina*[33].



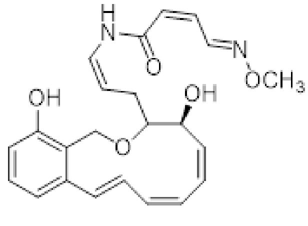
(+)-Dynemicin A

Camptothecin is an antitumor agent, isolated by wall et al. in the year 1966[34] and Sakato et al in 1974[35], from a Chinese plant *Camptotheca acuminate*. It inhibits cell division by inhibiting enzyme topoisomerase I. Suzuki coupling mediated synthesis of camptothecin derivatives was reported by wang et al. in 2014[36].



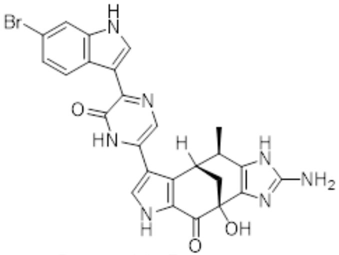
Camptothecin

Oximidine II is a benzolactone enamide, isolated from *Pseudomonas* sp. Q52002, in the year 1999 by Kim et al. [37] and was found to show activity towards vacuolar type ATP-ases, thus acting as anticancer agents, and as molecular targets for glaucoma, Alzheimer's disease, osteoporosis. Suzuki cross coupling for oximidine II was reported by Molander et al. in 2004[38].



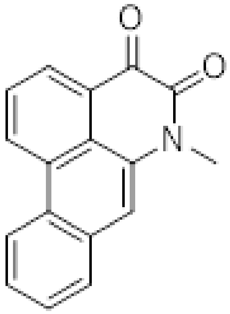
Oximidine II

The synthesis of Dragmacidin F, a bromoindole alkaloid, was reported by Garg et al. in 2004[39]. Dragmacidin F shows antiviral activity against HSV-1 and HIV-1 virus, and is biosynthesized in marine sponge *Dragmacidon* sp. Its isolation was reported in the year 1987 by Kohmoto et al[40].



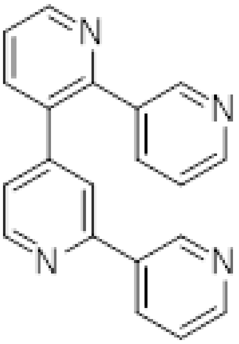
Dragmacidin F

Similarly, aporphines are the derivatives of quinoline alkaloids isolated from various plant species[41], have been found to show anti-tumor[42], dopaminergic[43], anti-parasitic and anti-platelet activity[44] along with vasorelaxing action. The synthesis of 4,5-Dioxo Aporphine via Suzuki-cross coupling reaction was reported by Suau et al[45].



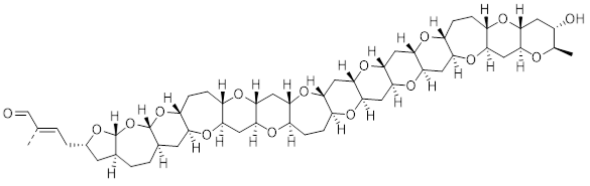
4,5-Dioxo Aporphines

Nemertelline, a neurotoxic tetra-pyridine compound, was isolated from *Amphiporus angulatus*, a hoplonemertine worm found in deep sea. The compound is used as an anti-fouling anent for boats and ships[46]. Suzuki-cross coupling reaction to synthesize quaterpyridine nemertelline was reported by Bouillon et al. in 2003[47].



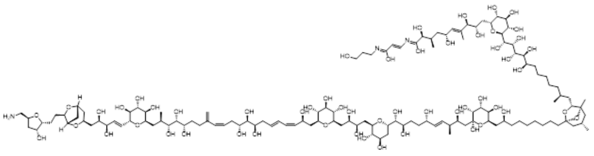
Nemertelline

Gymnocin A, a biggest natural polyether possessing cytotoxic properties, was isolated from dinoflagellate, *Gymnodinium mikimotoi*, found at Kushimoto Bay, in Japan[48]. Due to the presence of fused ring system, compound could be synthesized effectively via Suzuki reaction and was first reported in the year 2005[49].



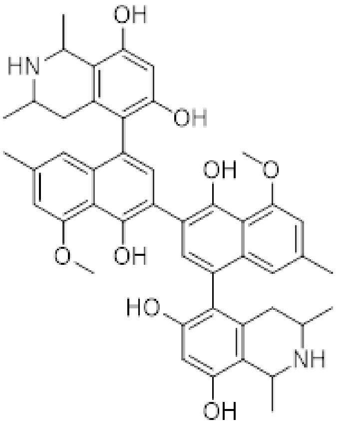
Gymnocin A

Palytoxin is a non-proteineceous, and the most toxic substance known to be found in corals *Palythoa* and dinoflagellates *Ostreopsis* found in tropic and sub-tropic seas. Compound was first isolated by Moore et al in 1971 from sea-weed "limu-make-o-Hana", as a non crystalline substance[50]. Suzuki based synthesis of palytoxin was reported in 1987 by Uenishi[51], and in 1989 by Kishi[52].



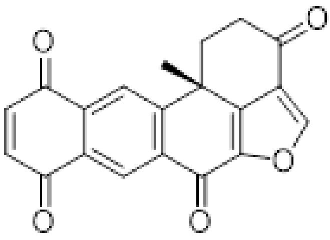
Palytoxin

An atropisomeric naphthylisoquinoline alkaloid, Michellamine, is a strong HIV replication inhibitor, isolated from leaves of *Ancistrocladus korupensis* found in Korup rainforest of Cameroon. Isolation was first reported by Boyd et al. in the year 1994[53,54]. First successful synthesis of compound was reported by Hoye et al. in 1999[55].



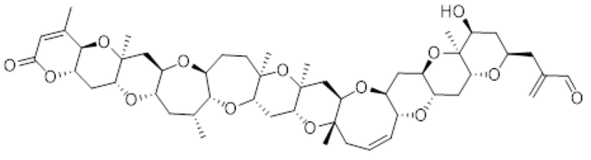
Michellamine

Halenaquinone, is a inhibitor of phosphatidylinositol-3-kinase. Drug was first isolated from a marine sponge *Petrosia alfiani* by Roll et al. in 1983[56]. Compound inhibits osteoclastogenesis, induced by RANKL, and secondary DNA binding of RAD51. The compound is also found to induce apoptosis in PC12 cells. Drug was synthesized by Kojima et al. in 1996[57].



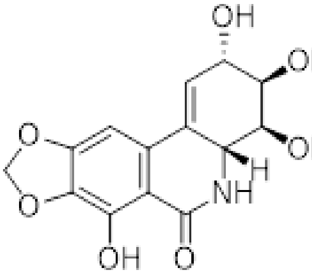
Halenaquinone

Brevetoxin, similar in structure to Gymnocin A, is a neurotoxic, polyether compound isolated from dinoflagellate *Karenia brevis*, by Lin et al in 1981[58]. Synthesis was reported by Nicolaou et al. in the year 1996[59].



Brevetoxin

Narciclasine, an antitumor agent, is an isocarbostyril alkaloid, biosynthesized in flowers of genus *Narcissus*. Compound was isolated by Ceriotti et al in 1967[60] and was known for inhibition of cell division. Drug was synthesized via Suzuki cross-coupling reaction by Hudlicky et al. in 1999[61].



Narciclasine

Apart from synthetic analogs of natural products, various synthetic compounds possessing pharmacological action have been prepared via Suzuki cross coupling reaction. Lapatinio, Merestinib, Rucaparib, Abermaciclib, Niraparib are anticancer agents, with lapatinio being a marketed drug and others in phase III clinical trials. Similarily, Ruxolitinib is used agant myelofibrosis, while, etoricoxib, flurbiprofen, felbinac, fenbufen, difunisal are antiinflammatory agents. Preclamol, dopaminergic agonist, is another drug prepared via Suzuki cross-coupling[63,64].

CONCLUSION

Suzuki-Miyaura cross coupling reaction is a versatile tool for C-C bond formation by coupling of boronic acid with organohalide, in the presence of palladium (0) as catalyst and a base. A wide range of alkenyl, aryl and heteroaryl halides can be coupled with alkenyl or aryl derivatives of boronic acids, and thus aids in synthesis of various synthetic and natural product analogs. At present Suzuki coupling aims at development of a recyclable catalyst with minimum amount of palladium, either in the form of nanoparticle or bound to a solid support the prevents leaching of metal.

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