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Chromatography with silver nitrate: part 2

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1. Introduction

The use of silver nitrate as a chromatography support to better facilitate difficult separations of organic compounds, is a technique that has been widely applied since Morris,[1] de Vries,[2] Dutton[3] and Barrett,[4] first realised the power of argentation chromatography in the 1960s. The underlying principle is based on silver acting as a π acceptor and engaging with a π donor contained within the molecule(s) to be separated, and those molecules that do not contain a π donor (or fewer π donors) will elute at a faster rate providing otherwise unattainable separation (e.g., alkane from an alkene). A

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number of review articles have been published, which detail to a greater extend the theory behind silver complexation,[5–7] and therefore these aspects will not be discussed in detail herein. It has been 15 years since our first review on this topic,[8] which has inspired us to provide an up-date covering the years 2001–2015.

A number of abbreviations are used in this article for various adsorbents containing silver nitrate (SN), SN impregnated upon silica gel (SNIS) and upon alumina (SNIA).

2. Natural product (NP) isolation

2.1. Hydrocarbon based NPs

In two separate biosynthetic studies Schulz[9] and Peters[10] reported the deployment of SNIS to isolate fusicoccadiene (**1**) and *ent*-isokaurene (**2**) (Fig. 1). Schulz demonstrated that access to preparative scale amounts of fusicoccane could be achieved through biosynthesis in microbial hosts (*Alternaria brassicicola*, *Aspergillus nidulans* and *Saccharomyces cerevisiae*); whereas, Peters investigated the rice (*Oryza sativa*) genome, which contains a family of kaurene synthase-like genes (OsKSL) involved in diterpenoid biosynthesis, and found that OsKSL5 and OsKSL6 produce *ent*-isokaur-15-ene (**2**).

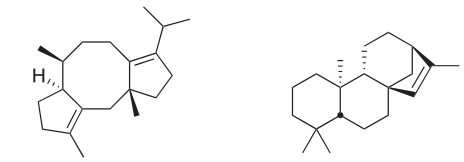


Fig. 1. Fusicoccadiene (**1**) and *ent*-isokaurene (**2**).

Further exploration in the biosynthetic realm by Faraldos and Coates[11] revealed that recombinant tobacco 5-*epi*-aristolochene synthase (TEAS), when fed (2*Z*,6*E*)-farnesyl diphosphate as an alternate substrate for TEAS, gave productive enzymatic cyclization to an array of products derived exclusively from the cisoid pathway. SNIS fractionation of extracts from preparative incubations was key to the outright separation of the cyclic sesquiterpenes; (+)-2-*epi*-prezizaene (**3**), (−)-α-cedrene (**4**), and (−)-β-curcumene (**5**) (Fig. 2). Bortolomeazzi et al.[12] reported that many cyclic sesquiterpenes from virgin olive oils were fractioned using SNIS.

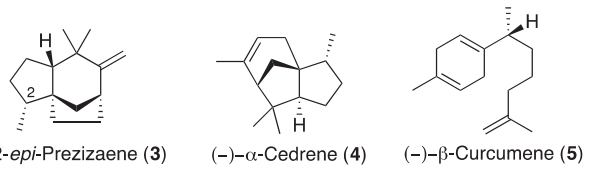


Fig. 2. *epi*-Prezizaene (**3**), α-cedrene (**4**), and β-curcumene (**5**).

Sandalwood, a parasitic plant distributed widely throughout South Asia and Australia, is popular for its essential oil, which is extensively utilised in aromatherapy. In the view that the major constituents of the East-Indian sandalwood oil [i.e., (*Z*)-α-(**6**) and (*Z*)-β-santalols (**7**) as a prelude to Section 2.2] are responsible for most of the observed biological activity, Thulasiram[13] undertook a study on the separation of this oil using SNIS. In conjunction with medium pressure liquid chromatography (MPLC) the separation of both α-(**8**) and β-santalenes (**9**) and (*Z*)-α-(**6**) and (*Z*)-β-santalols (**7**) was quantitatively achieved with SNIS using hexane and dichloromethane mobile phases (Fig. 3).

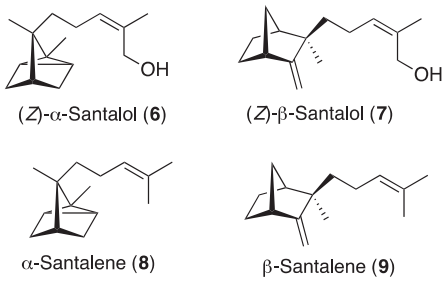


Fig. 3. Sandalwood essential oil components separated by SNIS.

2.2. Oxygen containing NPs

Long chain hydrocarbons containing various degrees of unsaturation have extensively benefitted from SN mediated purification.[14,15] Momchilova et al.[16,17] have been prolific in the area of fatty acid, lipid and triacylglycerol separation. Utilising SNIA Charkraborty[18] was able to purify eicosapentaenoic acid (**10**) derived from chemically hydrolyzed sardine oil (Fig. 4). Whereas, van Beek[19] required a silver loaded cation exchange HPLC column to achieve the separation of ginkgolic acids [e.g., C15:1 (**11**) and C17:1 (**12**)] using a methanol–water solvent system acidified with 0.1% formic acid (Fig. 4).

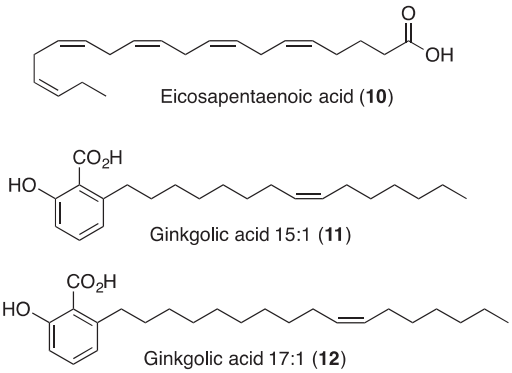
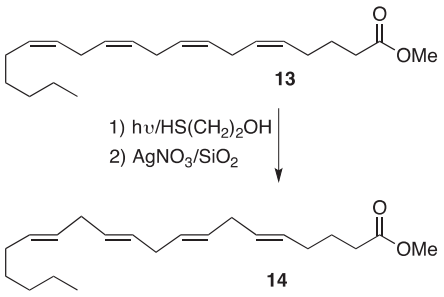


Fig. 4. Eicosapentaenoic acid (**10**) and ginkgolic acids (**11**) and (**12**).

In a related fatty acid study Ferreri and Chatgilialoglu extensively investigated whether thiyl radicals are responsible for *cis* to *trans*-double bond isomerization in various biochemical processes. For example, exposing all *cis* **13** to the thiyl radical and obtaining **14** after SNIS purification (Scheme 1).[20–27]



Scheme 1.

In a continuing program investigating medicinal plants from the native Bolivian flora, Sterner[28] discovered that the flowers of *Kaunia lasiophthalma* produce the linear bis-butenylide **15**, which was