tection of saturated hydrocarbons. In effect, these molecules yield neither UV nor fluorescence spectra under the usual analytical working conditions. Moreover, they have traditionally been considered inert molecules. However, in 1947 it was found (verified in 1981) that alkanes show a visible green fluorescence when eluted in a solution of berberine from a silica gel column (11,12). This phenomenon was applied to TLC by Marsh and Hiekane (13) in 1991 to detect saturated hydrocarbons in bitumen using berberine-impregnated silica gel plates, elution with *n*-hexane, and fluorescence scanning densitometry (λ_{exc} = 264 nm (see Sec. IV.B.1.c), However, this phenomenon was neither systematically studied nor applied to other products until 1999, when it was investigated by Cebolla and coworkers (14–16) (Fig. 1). They used 365 nm as excitation wavelength. They showed that the fluorescence intensity increases with the mass of alkane and the alkane chain length and that the fluorescent emission is due to a ion-induced dipole interaction between the berberine cation and the corresponding saturated hydrocarbon. This model allows the experimental results to be explained.

Although TLC is not efficient enough to molecularly separate all the saturated hydrocarbons in real samples, several methods have been proposed to separate and determine saturated hydrocarbons as a group (14). Likewise, it has also been possible to separate alkanes and isoalkanes from cycloalkanes, and determine both families, in middle distillates (17). Details of these methods are given in Section IV.B.1.c.

2. Alkenes and Terpene Hydrocarbons

Olefins are present in products derived from petroleum cracking, whereas terpene hydrocarbons are present in samples derived from natural products and organic reactions. Argentation chromatography in TLC is a well-known method for the separation of all these unsaturated compounds, as shown in Table 1. A review has been published on this useful technique (5). Argentation is carried out by spraying the plates with a saturated aqueous solution of silver nitrate; dissolving the silver salt in a solvent or a mixture of solvents in the desired concentration and then incorporating it in the silica gel slurry; inserting the edge of the plate into a solution of 10% aqueous silver nitrate, about 1 cm high, and allowing the solution to travel the length of the plate; and using developing solvents containing silver salt (18).

Silver nitrate–impregnated TLC plates were used to investigate cyclopentene and cyclohexene (19), and separation of allylic derivatives of benzene or cyclohexene from their propenylic isomers was also carried out (20). In this case the compounds studied were pulegone, isopulegone, estragole, anethole, eugenol, isoeugenol, safrole, and isosafrole. Only the allylic isomers formed complexes with silver nitrate, because the propenyl derivatives showed about the same R_f values on both silica and impregnated silica.

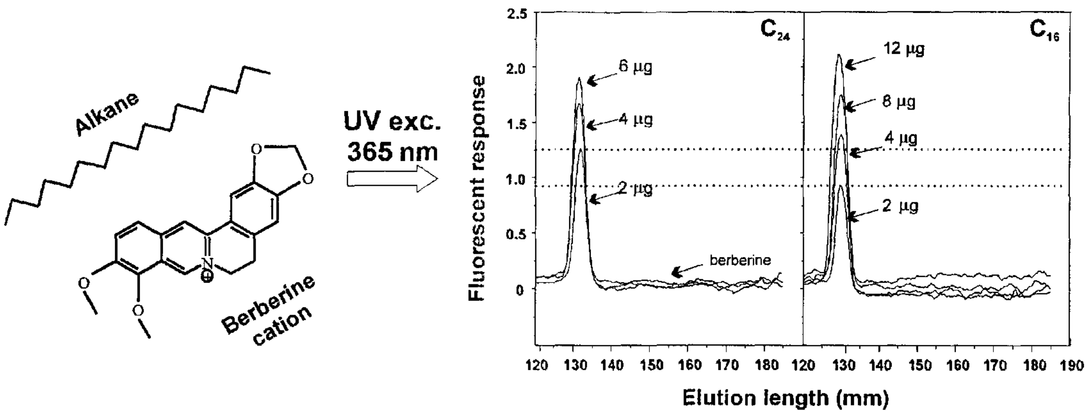

Figure 1 TLC chromatograms of *n*-C_{24} and *n*-C_{16} determined by enhancement of fluorescence response using berberine-impregnated silica gel plates (development: 9 min with *n*-hexane). (From Ref. 16. Copyright 2000 American Chemical Society.)