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Note

Chromatography of cashew nut-shell liquid

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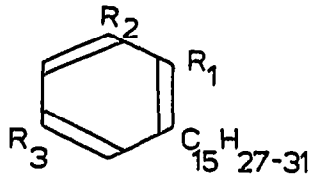
The separation of the components of cashew (*Anacardium occidentale* L.) nut-shell liquid (CNSL) by chromatographic techniques reported in the literature[1–4] could not be fully reproduced in our hands and is not satisfactory for the isolation of minor components of possible biological significance.



I

Anacardic acid (I, $R_1 = CO_2H$, $R_2 = OH$, $R_3 = H$) (ANA) behaves in a peculiar fashion on a silica gel G TLC plate developed with benzene–ethyl acetate (95:5). Contrary to its previously stated behaviour[1–4], the compound streaks along the plate, reaching the spot corresponding to cardanol (I, $R_1 = H$, $R_2 = OH$, $R_3 = H$), its decarboxylation product. A typical TLC plate is shown in Fig. 1, in which the behaviour of ANA and also a chromatographic separation of natural CNSL are shown. This behaviour was not observed by previous workers, perhaps as a consequence of the difficulty in localizing the presence of the compound by reaction with diazonium salts. The reactivity of ANA towards electrophilic substitution is very low and its presence is distinguished well only on aged plates. Spots due to minor amounts of decomposition products remained on the baseline and were therefore uncorrectly assigned to ANA. The use of bromophenol blue as developer is much more efficient in detecting the compound on the plates and serves to confirm that is is actually ANA that behaves in such way and not a decomposition product formed during the chromatographic process. We confirmed in fact that ANA is extremely stable even in the presence of strong acids. This observation is important because for the first time it enables one to confirm that the trace amount of cardanol found in the TLC analysis is really a natural component of CNSL.

From the evidence obtained so far, it is clear that a silica gel column is not ade-

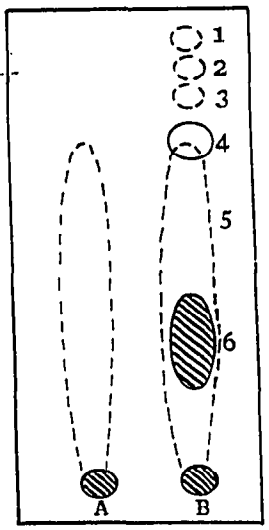


Fig. 1. Silica gel TLC of CNSL components. (A), Anacardic acid. (B), 1 and 2, low-polarity components; 3, anacardol; 4, phenolic component; 5, anacardic acid; 6, cardol.

quate for the separation of the components of natural CNSL. ANA begins to come off the column with solvents of very low polarity and we have been able to collect it in a pure form in a fraction coming out of the column prior to the dihydroxyphenol known[5] as cardol (I, $R_1 = H$, $R_2 = OH$, $R_3 = OH$).

In previously reported[2,3] chromatographic separations of CNSL on silica using as developing solvent a mixture of *n*-hexane–diethyl ether–formic acid, ANA was detected as a normal spot with an R_F value of 0.76 just in front of cardanol. We confirmed this result, and the observed stability of anacardic acid in the presence of acid removes any doubts that decarboxylation could have occurred under such conditions. Formic or acetic acid added in an amount of 2% to benzene–ethyl acetate produces similar results.

The abnormal behaviour of ANA on the silica gel plates requires some comment. We suggest that the streaked appearance of the compound results from an equilibrium established between an internal hydrogen bonded form which runs on the plate and a non-internally bonded form which does not move. The effect of small amounts of formic or acetic acid in the developing solvent can be ascribed to the formation of "mixed hydrogen-bonded dimers" with small-molecule adducts that tend to move on the plates. The small amount of acid required to promote such a dramatic change in the displacement of ANA is not sufficient to produce significant alterations in the R_F values of the non-carboxylic components.

An alumina column (Brockman, grade III) separates ANA cleanly from the remaining components of natural CNSL, and from the material recovered we observed that it constitutes *ca.* 70% of the crude natural product and not 90% as claimed earlier[5]. Once ANA has been separated from the other components, the latter are well separated on a silica gel plate, as shown in Fig. 2.

It is of interest that one of the components which we could isolate in a chromatographically pure form, directly from the alumina column seems to be a phenolic

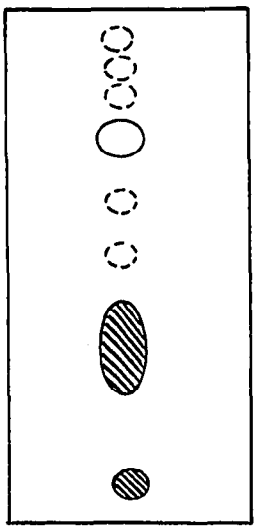


Fig. 2. Silica gel TLC of CNSL components excluding anacardic acid. Two extra possibly phenolic components can be seen.

compound detected previously[2–4] but, contrary to the statement in a recent paper[6], describing work in which the compound was isolated by a more laborious chromatographic technique, our compound shows a very strong carbonyl absorption at 1730 cm^{-1} prior to hydrogenation. Work on the characterization of this and other minor components of CNSL will be described elsewhere.

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