Raymond reaction. One of them had properties identical with those of dihydrocannogenol and the other is apparently a dihydrosecurigenol (III). Using preparative paper chromatography, these compounds were separated in the individual amorphous state and some of their properties have been established.

The difficulty of the hydrogenation of the double bond in ring A is probably due to steric hindrance. In view of the fact that Δ^4-steroids can exist in two spatial forms [6], rings A and B in securigenin may be illustrated by two conformational formulas—VI and VII. Depending on the form which the steroid exists in at the moment of hydrogenation, two different products may be obtained—form VI gives the 5α- and VII the 5β-compound. The formation of an intermediate ring between the surface of the catalyst and the compound undergoing reduction is possible only from the less screened side of the molecule. In securigenin this the front side (β-side) from which the approach of the catalyst is freer. In this case, the hydrogen at C_5 takes up the β-configuration, giving dihydrocannogenin [7].

Since the hydrogenation of securigenol in a neutral medium gives dihydrocannogenol (IV) and not dihydrocoroglaucigenin, the most probable conformation for securigenin is VII and not VI.

Thus, securigenin is 3β,14β-dihydroxy-19-oxocard-4,20:22-dienolide and securigenol is 3β,14β,19-trihydroxycard-4,20:22-dienolide. Their structures can be demonstrated by the conformational formulas VIII and IX.

A structure similar to that of securigenin has recently been proposed for hyrcanogenin [8]. Since the aglycone concerned was first isolated from Securigera securidaca [9] and full information on the determination of its structure are reported in the present paper, it appears to us to be right to retain for this compound the trivial name securigenin.

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STRUCTURE OF HELIANTHOSIDE C—A SAPONIN FROM THE SUNFLOWER

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The chromatography of an acid hydrolysate of helianthoside C [1] on paper and the photocolorometry of chromatograms of the sugars has shown that the monosaccharides of helianthoside C—glucose, arabinose, xylose, and rhamnose—are present in the saponin in a ratio of 2:1:1:3. The molecular weight of the glycoside determined from the yield of the aglycone is 1469.

The saponin and its acetate were treated with diazomethane and the reaction products were subjected to hydrolysis. In both cases, echinocystic acid was isolated, which shows the presence of a O-acyl glycosidic bond in the glycoside. An analysis of the products of the saponification of helianthoside C with alkali showed the presence of a glycoside coinciding in R_f value with helianthoside A.

By chromatography in a thin layer of silica gel and by gas-liquid chromatography the hydrolysate of helianthoside C methylated by Kuhn's method [2] was shown to contain fully methylated glucose, xylose, and rhamnose, 3,4-di-O-methylarabinopyranose, 2,3-di-O-methylrhamnopyranose, and 2,4-di-O-methylglucopyranose. The results of the methylation were confirmed by the periodate oxidation to saponin.

When the permethylated saponin was cleaved with lithium aluminum hydride, derivatives of an oligosaccharide and a glycoside were obtained. The latter was shown to contain completely methylated rhamnose and xylose and also

2,3-di-O-methylrhamnopyranose and 2,4-dimethylglucopyranose. The oligosaccharide was found to contain 2,3,4,6-tetra-O-methylglucose, 2,3-di-O-methylrhamnose, and 3,4-dimethylarabitol. Thus, the carbohydrate chain attached by the acyl glycosidic bond has the structure D-G_p1-4L-Rha_p1-2L-Ara_p1-.

When the saponin was heated with 0.12 N HCl (14 hr), a group of mono-, di-, and tetraglycosides of echinocystic acid was obtained.

The acid hydrolysis of the monoglycoside showed that a glucose residue is directly attached to the aglycone.

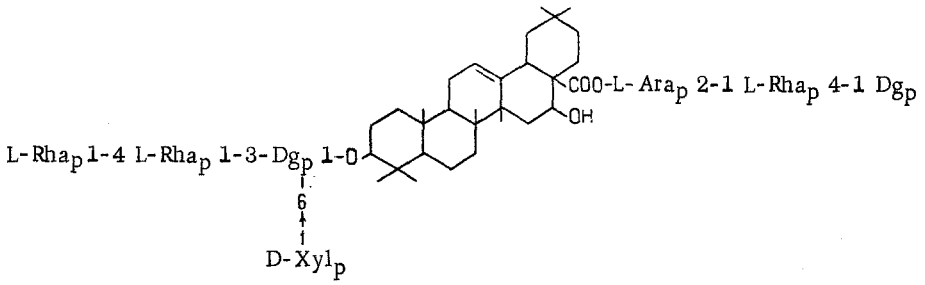
The diglycoside contained glucose and xylose. When the diglycoside was subjected to periodate oxidation, both sugars were decomposed, which excludes the possibility of a 1→3 bond between them. It was shown by methylation that the xylose residue is attached to the OH group of glucose in position 6.

When the tetraglycoside was hydrolyzed, glucose, xylose, and rhamnose were identified. Among the methylation products the same monosaccharides were found as in the lithium aluminum hydride decomposition of methylated helianthoside C.

Thus, the structure of the carbohydrate chain attached to the hydroxy group of echinocystic acid is expressed by the formula

$$LRha_p1 \rightarrow 4LRha_p1 \rightarrow 3D\,Gl_p$$
$$\uparrow 6$$
$$D\,Xy_p$$

Apparently, by analogy with other triterpene glycosides [3,4], this carbohydrate fragment is attached to the hydroxyl at C_3 of the aglycone and, therefore, the most probable structure of helianthoside C is expressed by the following formula:



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ISOLATION OF ALKALOIDS FROM THERMOPSIS ALTERNIFLORA

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This paper reports a method for the qualitative monitoring of the production of the alkaloids of Th. alterniflora [1] using thin-layer chromatography. For this purpose, alumina or grade KSK silica gel mixed with gypsum (9 : 1) were used. The mixture (layer thickness 25 μ) was deposited using the equipment described by Stahl [2], dried at 60-70° C for 4 hr, and chromatographed in chambers (D = 100 mm, H = 250 mm). The alkaloids were deposited in 8-12 γ portions to a total of 20-30 γ. The spots were revealed with Dragendorff's reagent. Several systems of solvents were investigated (table).

In the extraction of the alkaloids from the plant with water (time of steeping with one portion of solvent 24 hr, extractants used at the rate of 1 kg of plant to 4 l) it was found that the fourth extract no longer contained cytisine and