authentic sample of gardenoside pentaacetate [1] by IR and PMR spectroscopy (c) Acetate-3 (24 mg), colourless needles, mp 127–129°, $[\alpha]_D^{25}$ + 5.6° ($CHCl_3$, $c = 0.90$‡; ν_{max}^{KBr} cm^{-1}: 1740, 1660, 1630; PMR ($CDCl_3$) δ: 1.97–2.08 (5 × OCOMe), 4.71 (2H, *br. s*, 10-H), 5.83 (1H, *m*, 7-H), 7.17 (1H, *d*, J = 1.0 Hz, 3-H), 9.30 (1H, *s*, 11-H). (Found: C, 54.68; H, 5.91. Calcd. for $C_{26}H_{32}O_{14}$: C, 54.93; H, 5.67%). Acetate-3 was identical to an authentic sample of tarennoside pentaacetate [3] by IR and PMR spectroscopy.

Another portion (1.6 g) of the above residue was chromatographed on Amberlite IRA-410 (OH-type) with H_2O–AcOH with increasing AcOH content. On evaporation, the eluate with 0.6 M AcOH gave a residue (260 mg), which was then acetylated (Ac_2O–Py) and the product was purified by chromatography on Si gel with Et_2O as eluent to give Acetate-4 (46 mg) as an amorphous powder, $[\alpha]_D^{25}$ + 9.5° ($CHCl_3$, $c = 1.04$) lit. [4], $[\alpha]_D^{23}$ + 14.9° ($CHCl_3$, $c = 1.61$)); ν_{max}^{KBr} cm^{-1}: 1740, 1630; PMR ($CDCl_3$) δ: 2.02–2.08 (5 × OCOMe), 4.73 (2H, *br. s*, 10-H), 5.87 (1H, *m*, 7-H), 7.55 (1H, *s*, 3-H); (Found: C, 53.37; H, 5.62. Calcd. for $C_{26}H_{32}O_{15}$: C, 53.43; H, 5.52%). This substance was identical to an authentic sample of geniposidic acid pentaacetate [4, 5] by IR and PMR spectroscopy.

Although Briggs and Nicholls recorded a negative test for asperuloside in *Wendlandia luzoniensis* [6], we have now succeeded in isolation of four asperuloside-type iridoids from a plant of the same genus.

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TERPENES OF *SCHINUS TEREBINTHIFOLIUS*

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Key Word Index—*Schinus terebinthifolius*; Anacardiaceae; mono-, sesqui- and triterpenes.

Schinus terebinthifolius Raddi, which is native to Central and South America, was introduced to Florida 50 years ago as a shade and ornamental tree and spread rapidly to thousands of acres [1]. The suspected cause of allergies and respiratory afflictions, it is now considered a noxious species. Previous studies on fruits [2–4], leaves [5], and bark [5, 6] have revealed the presence of triterpene alcohols [5, 6], ketones [6] and acids [2–6]. However, the monoterpenes and sesquiterpenes have not been investigated; we now report on these and other terpenoid constituents.

Exhaustive hexane and ether extraction of crushed berries furnished two previously reported [2–5] triterpenes: masticadienoic and hydroxymasticadienoic acids, also a small amount of ursolic acid (comparison with authentic sample) and of an unidentified acid (MW 502). The neutral oily portion was examined by GLC (2 columns: 180 cm 1% OV-17 and 360 cm 10% SP-1000) and by GC–MS (same column packings). The bulk of the material (*ca* 80%) consisted of a mixture of 9 monoterpene hydrocarbons which were identified unambiguously by comparison with GLC R_t and MS spectra of authentic samples: α-pinene (25% of total monoterpenes), β-pinene (1%), sabinene (0.7%), Δ^3-carene (26%), α-phellandrene (16%), limonene (11%), β-phellandrene (8%), *p*-cymene (10%) and terpinolene (1%). The remainder of the oil, a complex mixture of over 50 components, consisted of monoterpene alcohols and ketones, sesquiterpene hydrocarbons, alcohols and ketones, and triterpene alcohols and ketones. *Cis*-sabinol, carvotanacetone, β-caryophyllene, α- and β-cubebene were identified by comparison with reported MS spectra. Simiarenol, simiarenone, α-amyrin and α-amyrenone were also identified by comparison with authentic samples. The large concentration of volatile monoterpenes (over 10% of the weight of air dried berries) may

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well be the cause of the respiratory ailments associated with the crushed fruits. These volatiles may also be excreted from the flowers as widespread respiratory distress occurs when the tree is in bloom [1].

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TWO FURTHER EREMOPHILANE DERIVATIVES FROM *TESSARIA ABSYNTHIOIDES*

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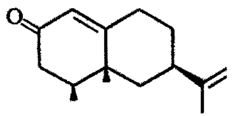
Key Word Index—*Tessaria absinthioides*; *T. integrifolia*; Inuleae; Compositae; new eremophilene derivatives.

From *Tessaria dodoneifolia* (H. et A.) Cabr. a flavanone [1] and from *T. absinthioides* (H. et A.) DC the eremophilene tessaric acid (**1**) [2] has been isolated. A reinvestigation of the latter species affords two further eremophilenes, their structures being elucidated by spectroscopic methods. All data are in agreement with the given structures. The retro-Diels–Alder-fragmentation observed in the mass spectra of **2** and **3** establishes the position of the ring double bond and with that also the position of the methyl groups. Though the absolute configuration was not established, the one given in the Scheme is that of all known compounds of this type.

In addition the thiopheneacetylene **5** [3] and the known eudesmane derivative carrissone (**6**) [4] were isolated. The structure of **6** was confirmed by dehydration to **7**. Tessaric acid however was not found.



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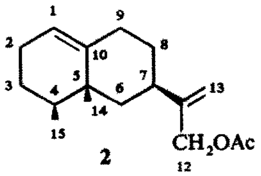

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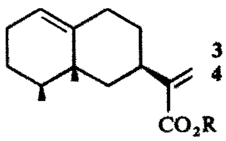

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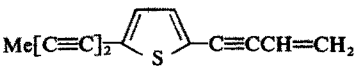
4: R = Me



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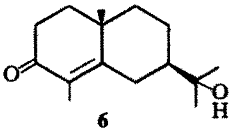

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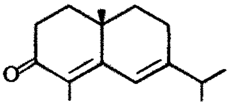

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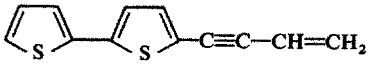

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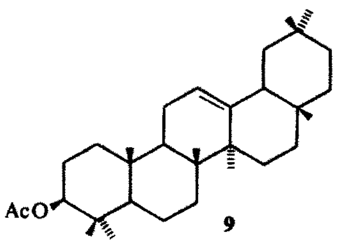

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* Part 103 in the series 'Naturally Occurring Terpene-Derivatives', part 102: Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 780.