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Editors

S.C. BHATTACHARYYA

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New Delhi, India, 12-16 November, 1989*

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Foreword

It is now possible to isolate the odorous constituents of a plant or an animal product by using different kinds of solvents under different sets of conditions or by using the established method of steam/hydro-distillation. Using a combination of newer analytical and instrumental techniques which have come up in recent years it is also possible to identify and characterize almost all the constituents present. The results have been amazing. In this chromatograph, gas-liquid chromatography and mass spectrometry have played eminent roles. The comparatively traditional methods of spectrophotometry have also gained added importance.

A large number of papers involving isolation, characterization and structure determination of the constituents of the odorous principles are being presented in this volume. Some of the papers are truly outstanding. As many of these papers as possible within the permissible time-frame have been accommodated in this volume. There is an overflow of good papers in this area and some of these have been shifted to the next volume dealing with Synthesis.

Participants to the Congress will find this volume very attractive and informative. They will know more about things which they have handled for ages. After going through this volume there will be reason for everyone to feel that there are more things in heaven.

PROF. S.C. BHATTACHARYYA
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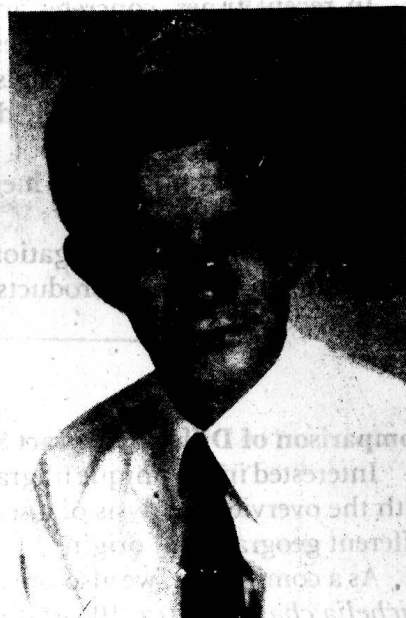
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New Volatile Constituents of the Flower Concrete of *Michelia champaca* L.

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ABSTRACT

The investigation of concrete samples of the flowers of *Michelia champaca* L. allowed us to identify a series of minor and trace constituents not yet known as natural products. Discussed in more detail are two dimethyl-pentylisoxazoles, two isoxazoles derived from β -ionone oxime and two hydroquinolines possibly derived from dihydro- β -ionone oxime. Besides the oximes mentioned above, some of the concretes contain many further oximes, which might be formed by transoximation of phenylacetaldoxime with corresponding carbonyl compounds present in the same substrate. Furthermore, a series of mono- and bicyclic ionone derivatives are discussed.

INTRODUCTION

Michelia champaca L. is a medium-size tree of the *Magnoliaceae* family native to the temperate Himalaya which, however, has found a wide distribution throughout the subtropical and tropical eastern hemisphere, from India and South China to Indonesia, the Philippines and the Pacific Islands. Its beautiful yellow flowers emit a very intense fragrance which might be verbally described as reminiscent of the orange flower, *Jasminum sambac*, carnation and ionones, especially β -ionone including derivatives.

Michelia champaca—often just named champaca—certainly belongs together with the closely related white-blooming *Michelia alba*, several *Plumeria* species and *Jasminum sambac* to the most famous fragrant flowers of southeast Asia, all enjoying also a high cultural image in this region. Thus, the champaca tree is highly venerated by the Hindus, who dedicated it to their god "Vishnu" and it is said that a blue champaca is blooming in the empyrean before Brahma.

In India and Indonesia, "attars of champaca" obtained by extracting the flowers with vegetable oils are already in use locally since a long time.

In recent times, concretes and absolutes of *Michelia champaca* have become commercially available as expensive specialities for the creation of high-class fragrances. They represent dark yellow to orange waxy materials or viscous liquids, respectively, which, in case of a genuine product, reflect to an acceptable degree the attractive fragrance of the fresh flower.

Up to now, only 1, 8-cineol, benzaldehyde, benzyl alcohol, phenylethyl alcohol, isoeugenol and methyl anthranilate are mentioned in the literature as fragrant constituents of *Michelia champaca* [1, 2].

During our own investigation, a series of structurally and olfactorily interesting compounds not yet known as natural products attracted special attention. Their discussion is the main subject of this paper.

EXPERIMENTAL

Comparison of Different Extract Samples of *Michelia champaca*

Interested in the unique fragrance concept of this *Michelia* species, we started our investigation with the overview analysis of a series of commercially available concrete and absolute samples of different geographical origins.

As a completion, we also prepared an own concrete by solvent extraction of 50 fresh flowers of *Michelia champaca* (ca. 100 g) collected in Jakarta (April 1985). The concrete thus obtained (110 mg) reflected well the pronounced ionone-floral scent of the living flower. All these samples have been cleaned-up by micro-distillation (up to 160°C, 0.02 Torr) prior to their investigation by combined GC-MS measurements (UCON 50 m and DB-Wax 30 m).

Table 1 lists the approximative percentage values of a selection of major and main constituents for an absolute sample and two concrete samples (concrete 1, concrete 2) all of Indian origin as well as for the concrete prepared by ourselves (concrete 3).

Although these samples of different origins are based on a common qualitative profile—also regarding minor constituents—their quantitative compositions differ considerably; in the case of concrete 3 even dramatically. Special attention attracts the dramatic difference in the ionone content of concrete 2 (~1.0%) and concrete 3 (~41%) as well as the fact, that the oximes of these ionones could only be identified in the absolute sample and in concrete 2. Worth mentioning are also the drastic differences in the contents of linalool, the *cis*-linalool oxide (pyranoid), phenylethyl alcohol, methyl anthranilate and indole. The reason for these quantitative differences might be, that these extract samples of *Michelia champaca* have been prepared from distinct sub-species. This point could not be clarified yet. As a contrast to the small concrete sample prepared by ourselves (concrete 3), we decided to use concrete 2 for the thorough investigation.

Pre-separation of Concrete 2

Flash distillation of 300 g concrete of *Michelia champaca* (ex Indian Aromatics, Crop 1983) furnished 174, 4 g of volatiles (bp. up to 160°C/0.05 Torr) which could be combined to the four distillation ranges shown in table 2. Concentrating our interest on the unknown constituents, these distillation ranges were separated by silica gel column chromatography using a hexane/ether

Table 1. Comparison of various extract samples of *Michelia champaca* (selection of major and main constituents)

Compound	Absolute ^a %	Concrete 1 ^b %	Concrete 2 ^c %	Concrete 3 ^d %
Linalool	2	0.2	0.8	11
Methyl benzoate	1	1	5	1
Benzyl acetate	4	0.1	0.6	0.05
Photoisomer of β -ionone ^e	0.1	0.1	< 0.1	0.5
cis-Linalool oxide (pyranoid)	0.2	0.6	2.5	7
Benzyl alcohol	0.8	0.3	2	0.1
Phenylethyl acetate	2	0.4	0.4	0.05
Phenylacetoneitrile	1.3	4.3	1.2	0.1
Phenylethyl alcohol	25	34	30	2
α -Farnesene	1.6	0.6	0.8	0.1
Dihydro- β -ionone	1.4	0.3	0.3	10
α -Ionone	1.6	0.2	0.05	6.8
β -Ionone	3.4	0.8	0.2	20
β -Ionol	0.3	0.1	0.03	0.8
Dihydro- β -ionol	1.1	0.3	0.4	3.8
Eugenol	0.2	0.7	0.7	0.2
Methyl anthranilate	4.5	2.1	9	1.4
Phenylacetaldoxime	0.5	1	1	0.1
Indole	2.9	12	4	2.5
Methyl (Z)-jasmonate (trans/cis. ~2:1)	0.6	0.3	0.2	0.3
Methyl palmitate	3	3	2	trace
Oximes of ionones	2	-	3	-
Methyl linoleate	13	18	10	t

^a ex Encece Aromatics Ltd., India, Crop 1983^b ex Encece Aromatics Ltd., India, Crop 1984 (so-called Simhachala variety)^c ex Indian Aromatics, India, Crop 1983^d prepared ourselves (1985)^e based on GC integration^f 2, 5, 5, 8a-Tetramethyl-6, 7, 8, 8a-tetrahydro-5H-1-pyran**Table 2.** Pre-separation of the concrete 2

Distillation	Range/0.05 Torr	Amount	Main constituents
1	-70°	51.4 g (17.1%)	linalool oxides, linalool, methyl benzoate, benzyl alcohol, phenylethyl alcohol, phenylacetoneitrile, ionones
2	70°-120°	34.6 g (11.5%)	ionones, methyl anthranilate, eugenol, cinnamic alcohol, indole, phenylacetaldoxime
3	120°-140°	63.0 g (21.0%)	oxygenated ionones, oximes of ionones, benzyl benzoate, methyl linoleate
4	140°-160°	25.4 g (8.5%)	high boiling fatty acids incl. methyl esters

gradient from 40:1 to 1:1. The individual fractions were checked by GC and afterwards the representative ones were thoroughly investigated by GC-MS measurements (capillary columns: UCON 50 m, DB-Wax 30 m). Olfactory information on unknown constituents could be obtained by sniffing at the exit of the capillary column during the GC run of the respective fraction. Finally, the unknowns were isolated as far as possible by preparative GC or preparative capillary GC, respectively, in order to elucidate their structures by spectroscopic means.

Applying these methods, about 240 constituents could be identified in this concrete, from which a selection is listed together with the respective peak numbers in the legend of figure 1 showing its overview gas chromatogram. The numbers in parentheses refer to their structures given in one of the following figures.

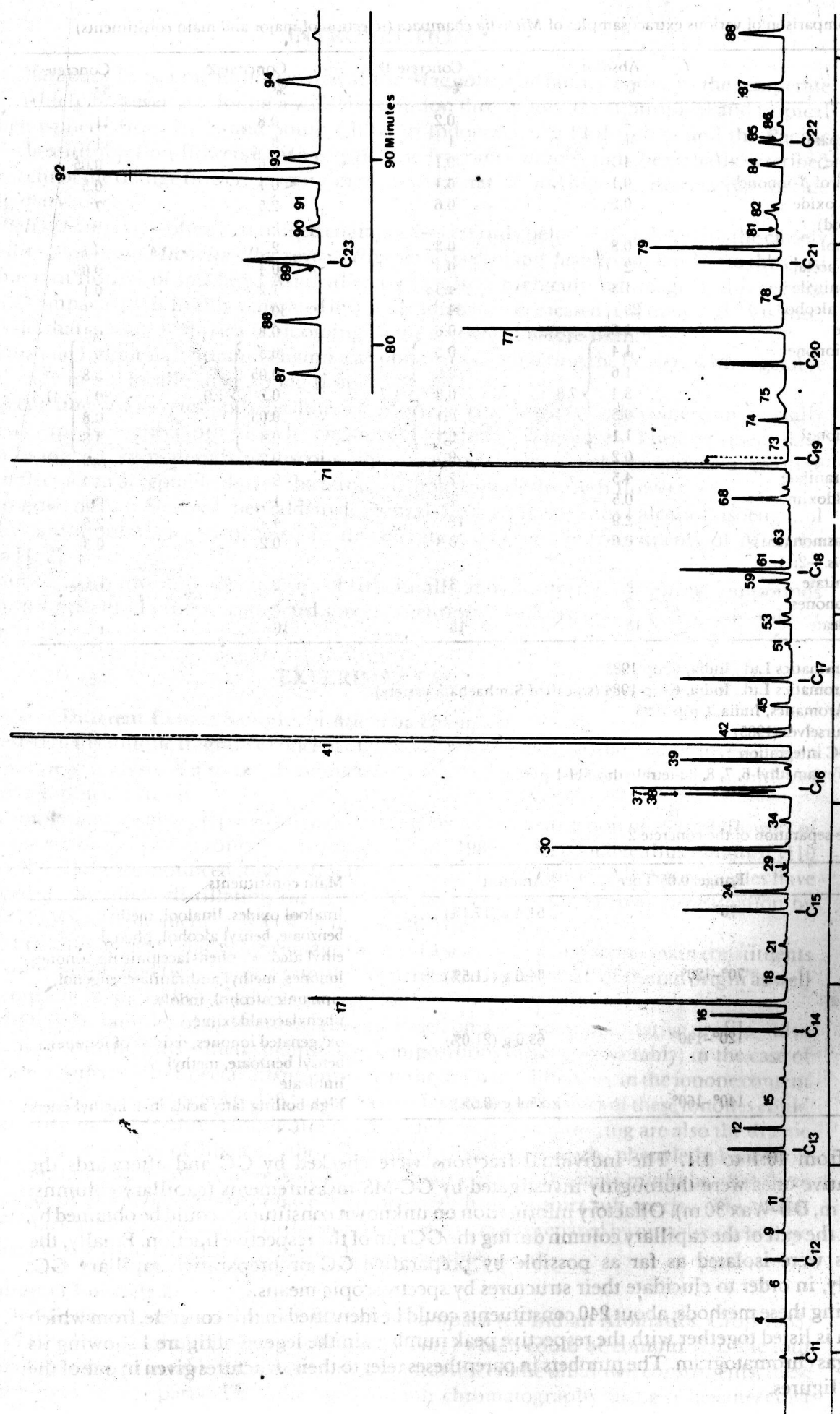


Figure 1. Gas chromatogram of concrete 2. UCON, 50 m x 0.3 mm i.d., 60° to 190° with 2.5°/min

1. 3-methylbutyronitrile; 2. β -pinene; 3. limonene; 4. 1, 8-cineol; 5. 3-methyl-1-nitro-butane; 6. trans-ocimene; 7. (Z)-3-hexenyl acetate; 8. 6-methyl-5-hepten-2-one; 9. n-hexanol; 10. (Z)-3-hexenol; 11. methyl 2-hydroxy-3-methylbutyrate; 12. cis-linalool oxide (furanoid); 13. methyl 2-hydroxy-3-methylvalerate; 14. 2-methylbutyraldoxime (E+Z, 14); 15. 3-methylbutyraldoxime (E+Z, 15); 16. linalool; 17. methyl benzoate; 17. theaspirane A (43a); 18. 1, 2, 5, 5-tetramethyl-octahydroquinoline (32); 19. theaspirane B (43b); 20. benzyl formate; 21. ethyl benzoate; 22. phenylacetaldoxime O-methyl ether (E+Z); 23. 2-undecanone; 24. benzyl acetate; 25. methyl (E)-3-methyl-4-decenoate; 26. α -terpineol; 27. methyl nicotatate; 28. 2, 5, 5, 8a-tetramethyl-6, 7, 8, 8a-tetrahydro-5H-1-benzopyran (42); 29. 2, 5, 5-trimethyl-5, 6, 7, 8-tetrahydroquinoline (31); 30. methyl phenylacetate; 31. cislinalool oxide (pyranoid); 32. phenylethyl formate; 33. methyl salicylate; 34. trans-linalool oxide (pyranoid); 35. 5-amyl-3, 4-dimethylisoxazole (1); 36. 3-amyl-4, 5-dimethylisoxazole (2); 37. benzyl alcohol; 38. phenylethyl acetate; 39. phenylacetone nitrile; 40. (E)-3-methyl-4-decen-1-ol; 41. phenylethyl alcohol; 42. trans- α -farnesene; 43. 6-methyl-5-hepten-2-one oxime ((E+Z)); 44. dihydro- α -ionone (17); 45. dihydro- β -ionone (35); 46. α -ionone (18); 47. trans-geranylacetone; 48. jasmone (26); 49. dihydro- β -ionyl formate (37); 50. α -ionol; 51. isoamyl benzoate; 52. epi-cubanol; 53. β -ionone (10); 54. β -ionol (33); 55. β -ionone 5, 6-epoxide (39); 56. cubanol; 57. 3-methyl-5-(2, 6, 6-trimethyl-cyclohex-1-en-1-yl)-isoxazole (12); 58. 1-nitro-2-phenylethane; 59. dihydro- β -ionol (36); 60. 7-oxo-dihydrotheaspirane A₁ (48a); 61. 7-oxo-dihydrotheaspirane B₁ (48c); 62. methyl N-methyl anthranilate; 63. caryophyllene epoxide; 64. methyl N-ethyl anthranilate; 65. 1, 3, 7, 7-tetramethyl-2-oxabicyclo [4.4.0] decan-9-one (49); 66. 7-oxo-dihydrotheaspirane A₂ (48b); 67. 7-oxo-dihydrotheaspirane B₂ (48d); 68. eugenol; 69. nerolidol; 70. trans-cinnamyl acetate; 71. methyl anthranilate; 72. benzaldoxime (24); 73. dihydrobovolide (8); 74. cinnamic alcohol; 75. phenylacetaldoxime (E+Z, 16); 76. isoeugenol; 77. indole; 78. methyl (Z)-jasmonate (trans:cis=2:1); 79. methyl palmitate; 80. dihydro- α -ionone oxime (E+Z, 17); 81. dihydro- β -ionone oxime (E+Z, 19); 82. 4, 4a, 5, 6-tetrahydro-4, 4, 7-trimethyl-2(3H)-naphthalenone (48); 83. α -ionone oxime (Z, 18); 84. α -ionone oxime (E, 18); 85. 3-oxo-dihydro- α -ionone (45); 86. β -ionone oxime (Z, 11); 87. β -ionone oxime (E, 11); 88. benzyl benzoate; 89. 3-oxo-dihydro- α -ionone (47); 90. methyl stearate; 91. 4-oxo-dihydro- β -ionone (46); 92. methyl linoleate; 93. phenylethyl benzoate; 94. methyl linolenate; (C₁₁-C₂₃ = corresponding n-alkanes, probably arising from solvent used for manufacturing the concrete).

RESULTS AND DISCUSSION

Isoxazoles

The champaca concrete contains several heterocyclic compounds, which may be considered as being derived from oximes.

The first two representatives could be enriched in fractions obtained by column chromatography of the first distillation range (hexane/ether 20:1).

The mass spectra of both compounds (figure 2) are characterized by a similar fragmentation and an elementary composition of the molecular ion of C₁₀H₁₇NO. Besides the rather non-specific ion series from m/z 152 to m/z 96, a prominent rearrangement ion at m/z 111 is observed in both cases. This could be taken as an indication for a dimethyl-pentyl-oxazole or a related isoxazole.

The somewhat more polar compound with slightly shorter retention time could be isolated by preparative GC in mg amount and the NMR data have been compatible with the structure of the 5-amyl-3, 4-dimethylisoxazole (1) (figure 3). Based on this information, the structure of the 3-amyl-4, 5-dimethylisoxazole (2) appeared likely for the second compound. The percentage values noted in parentheses beneath the corresponding formulae in figure 3 as well as in the following figures refer to their contents in the distillable part of the concrete investigated.

The structural proof for the new isoxazoles 1 and 2 was given by converting the α , β -unsaturated ketoximes 4 and 6, respectively, with iodine-potassium iodide in aqueous tetrahydrofuran in the presence of bicarbonate, as described by Büchi and Vederas [3] for comparable cases (figure 3).

The ketoximes 4 and 5 have been obtained from the easily accessible ketones 3 and 4 by reaction with hydroxylamine hydrochloride in the presence of pyridine in ethanol.

The 5-amyl-3, 4-dimethylisoxazole (1) shows a characteristic green-herbaceous odour reminiscent of estragon, celery and jasmone while the green-herbaceous character of the 3-amyl-4, 5-dimethylisoxazole (27) is modified by anis-like and nutty aspects.

Neither 1 nor 2 are known from literature. Up to now, the 4, 5-dimethylisoxazole identified in tomato [4] is the only representative of this structural class described as natural occurring.

It may be assumed that the natural formation of the isoxazoles 1 and 2 follows an analogous sequence from the ketones 3 and 5 to the oximes 4 and 6, respectively, which finally cyclize under oxidative conditions.

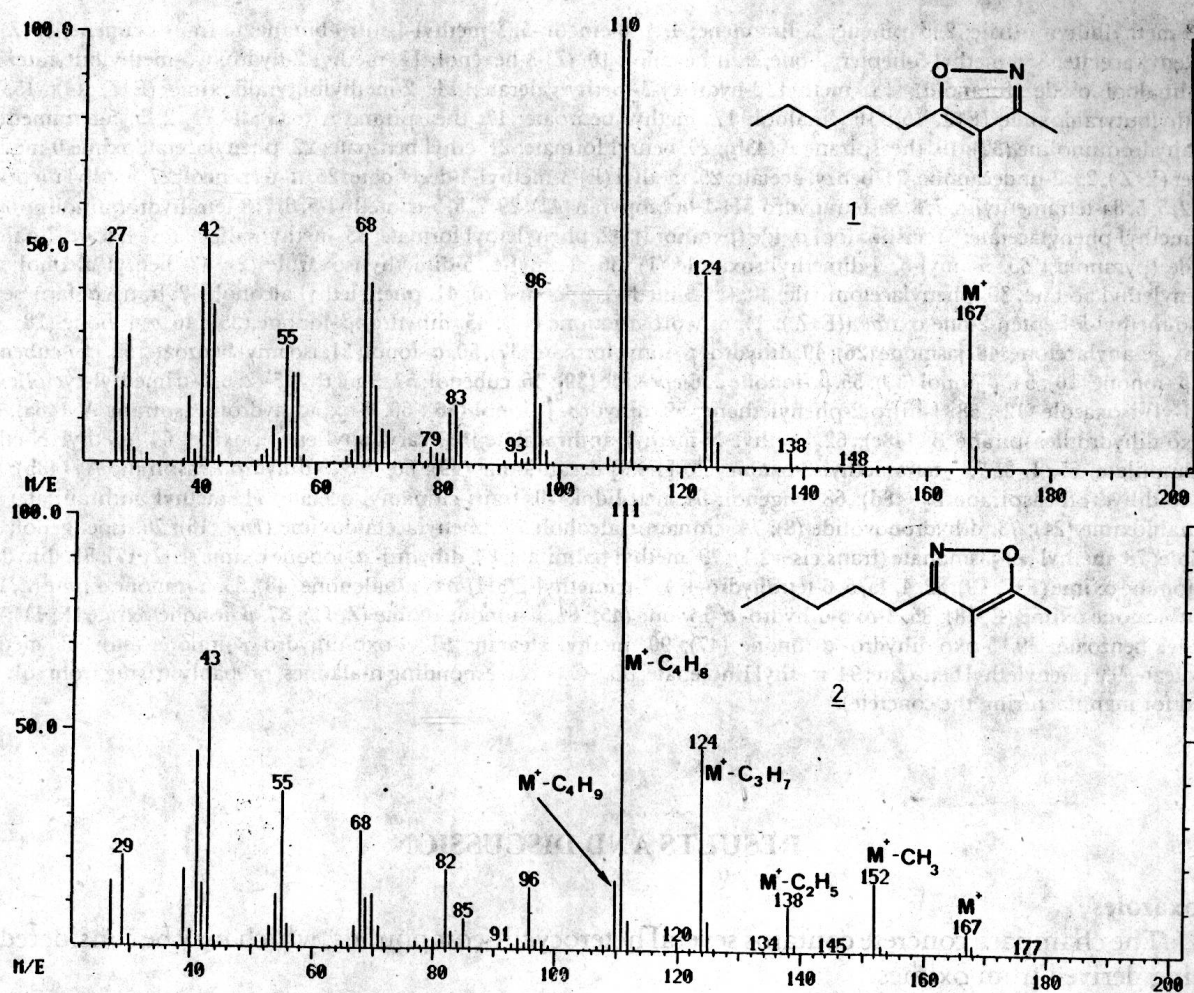


Figure 2. Mass spectra of 1 and 2

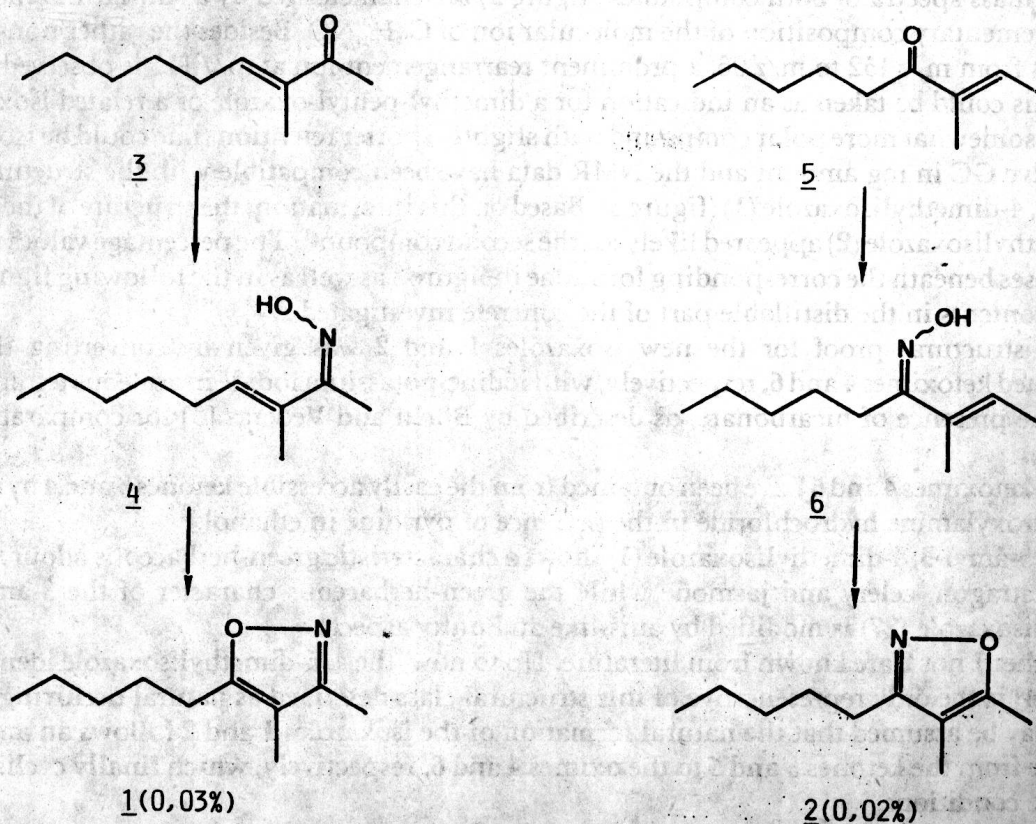


Figure 3. Isoxazoles 1 and 2

Indeed, the 3-methyl-2(E)-nonen-4-one (**5**) (figure 4) known as occurring in Oriental tobacco [5] is also a trace constituent of the champaca concrete. As stated by Demole [5] this unusual ketone could possibly be formed either by cross-aldol condensation between acetaldehyde and 3-octanone, or via hydration of bovolide and decarboxylative elimination of the hypothetical intermediate thus formed.

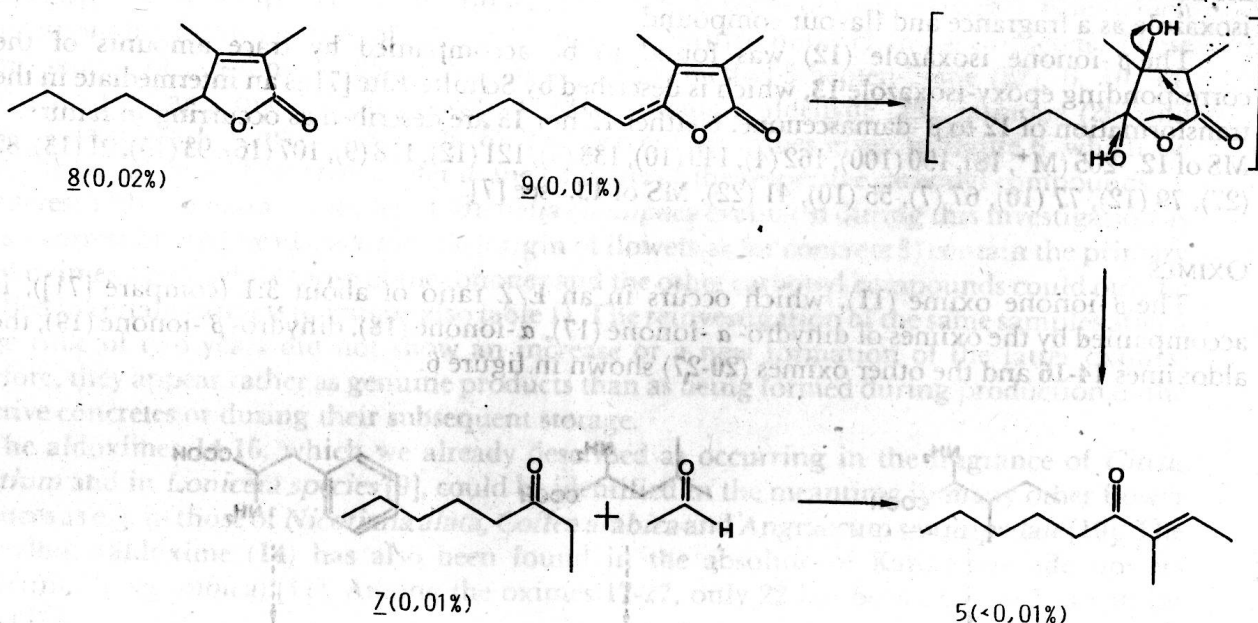


Figure 4. Possible formation of 3-methyl-2(E)-nonen-4-one (**5**)

Both possible precursors for **5**, the bovolide (**9**)—accompanied by its well-known dihydroderivative **8**—as well as the 3-octanone (**7**) could be identified in the concrete investigated. However, neither the ketone **3** nor the oximes **4** and **6** (figure 3) have been found.

Spectral data of **1** and **2**

1.—IR: 1637, 1460, 1422, 1388, 1378, 1163, 1112, 1060, 1010, 902 cm^{-1} .— ^1H -NMR (400 MHz): 0.89 (t, J~7, 3H); 1.31 (m, 2 \times 2H); 1.65 (m, 2H); 1.87 (s, H_3 , C-C(4)); 2.19 (s; H_3 , C-C(3)); 2.63 (t, J~7, 2H) δ ppm. -MS.: 167 (M^+ , 34), 138 (3), 124 (44), 111 (98), 110 (100), 96 (41), 83 (14), 82 (12), 69 (42), 68 (53), 57 (21), 56 (21), 55 (27), 43 (37), 42 (52), 41 (40).

2.—IR.: 1640, 1455, 1385, 1374, 1195, 1090, 1027, 975, 896 cm^{-1} .— ^1H -NMR (400 MHz). 0.90 (t with fine structure, J~7, 3H); 1.35 (m, 2 \times 2H); 1.65 (m, 2H); 1.87 (s, H_3 , C-C(4)); 2.28 (s, H_3 , C-C(5)); 2.55 (t, J~7, 5, 2H) ppm. -MS.: 167 (M^+ , 5), 152 (16), 138 (10), 124 (46), 111 (100), 110 (16), 96 (14), 82 (18), 68 (27), 55 (36), 43 (65), 41 (45).

Much clearer appears the formation of another isoxazole (**12**) (figure 5) isolated from the second

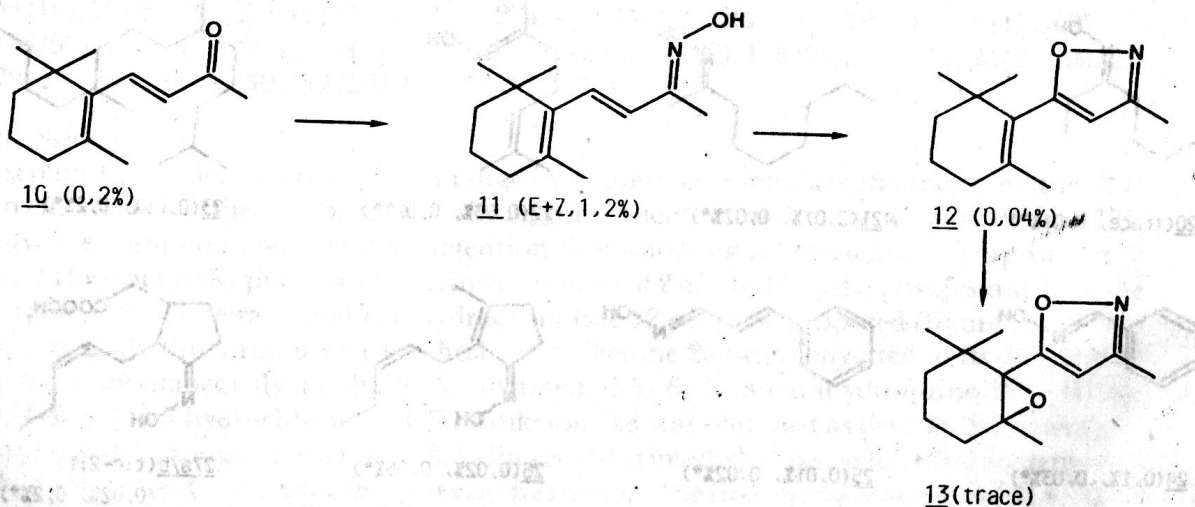


Figure 5. Isoxazoles **12** and **13** derived from β -ionone

distillation range (hexane/ether 20:1, preparative GC), since the corresponding ketone (10) and oxime (11) represent major constituents of the concrete. It could be identified as the 3-methyl-5-(2,6,6-trimethyl-cyclohex-1-en-1-yl)-isoxazole (12, β -ionone isoxazole), the well-known intermediate in the Büchi-Vederas transformation [3] of β -ionone (10) to β -damascone. It is characterized by an attractive ionone-floral odour accompanied by typical tobacco aspects and a patent [6] claims this isoxazole as a fragrance and flavour compound.

The β -ionone isoxazole (12) was found to be accompanied by trace amounts of the corresponding epoxy-isoxazole 13, which is described by Schulte-Elte [7] as an intermediate in the transformation of 12 to β -damascenone. Neither 12 nor 13 are described as occurring in nature. MS of 12: -205 (M^+ , 18), 190 (100), 162 (4), 149 (10), 133 (3), 121 (12), 118 (9), 107 (16), 93 (15), 91 (13), 82 (27), 79 (12), 77 (10), 67 (7), 55 (10), 41 (22). MS of 13: -see [7].

OXIMES

The β -ionone oxime (11), which occurs in an E/Z ratio of about 3:1 (compare [71]), is accompanied by the oximes of dihydro- α -ionone (17), α -ionone (18), dihydro- β -ionone (19), the aldoximes 14-16 and the other oximes (20-27) shown in figure 6.

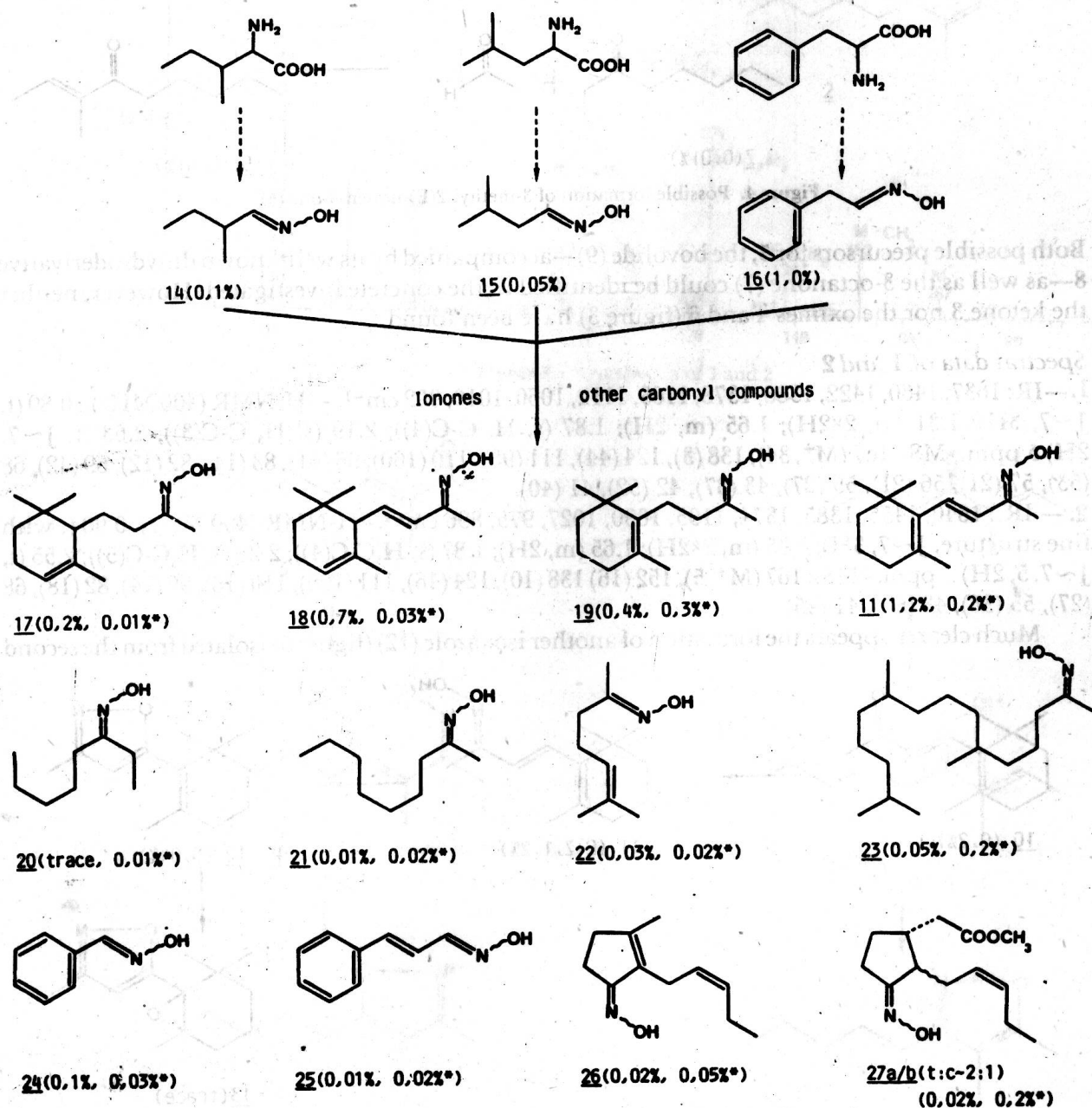


Figure 6. Oximes identified in concrete 2

While the 2-methylbutyraldioxime (14), the 3-methylbutyraldioxime (15) and the phenylacetaldoxime (16) are most likely derived from the corresponding amino acids isoleucine, leucine and phenylalanine (compare [9] and lit. cited therein), the ionone oximes 11 and 17-19 are possibly formed by transoximation of these primary formed oximes with the respective ionones.

This hypothesis is supported by the presence of a whole series of further oximes, from which the corresponding carbonyl compounds could also be identified in the champaca concrete. These are the oximes of 3-octanone (20), 2-nonanone (21), 6-methyl-5-hepten-2-one (22), 6, 10, 14-trimethylpentadecan-2-one (23), benzaldehyde (24), cinnamic aldehyde (25), jasmone (26) and methyl (Z)-jasmonate (trans:cis=2:1, 27a/b). The percentage values given in figure 6, which we additionally marked with asterisks, refer to the contents of the respective carbonyl compounds.

Interestingly, all extract samples of *Michelia champaca* evaluated during this investigation as well as a corresponding headspace sample (origin of flowers as for concrete 3) contain the primary formed oximes 14-16, while those of the ionones and the other carbonyl compounds could only be identified in certain extracts (compare also table 1). The reinvestigation of the same samples after a storage time of two years did not show an increase or a new formation of the latter oximes. Therefore, they appear rather as genuine products than as being formed during production of the respective concretes or during their subsequent storage.

The aldioximes 14-16, which we already described as occurring in the fragrance of *Citrus aurantium* and in *Lonicera species* [9], could be identified in the meantime in many other flower fragrances as e.g. in those of *Nicotiana glauca*, *Coffea arabica* and *Angraecum sesquipedale* [10]. The 2-methylbutyraldioxime (14) has also been found in the absolute of Karo-Karoude flowers (*Leptactinia senegambica*) [11]. Among the oximes 17-27, only 22 has been described as natural product [9].

Mass spectra of the oximes 11 and 17-27

11. 207 (M^+ , 2), 193 (13), 192 (100), 176 (5), 160 (37), 144 (3), 134 (6), 120 (6), 105 (6), 91 (11), 77 (8), 67 (4), 53 (5), 41 (11). - 17. - 209 (M^+ , 1) 194 (3) 192 (2), 177 (12), 161 (2), 137 (67), 121 (16), 109 (10), 98 (8), 95 (24), 93 (23), 86 (68), 81 (63), 79 (43), 73 (100), 67 (16), 55 (23), 41 (41). - 18. - 207 (M^+ , 34), 192 (15), 190 (12), 160 (4), 151 (80), 136 (100), 134 (65), 124 (37), 119 (18), 107 (23), 93 (74), 91 (34), 77 (27), 67 (14), 53 (15), 42 (34), 41 (34). - 19. - 209 (M^+ , 7), 194 (14), 192 (10), 177 (27), 161 (14), 137 (64), 121 (28), 105 (15), 95 (57), 93 (32), 86 (20), 81 (75), 79 (30), 73 (100), 69 (30), 55 (30), 41 (48). - 20. - 144 (M^+ + H, 144), 126 (2), 114 (14), 100 (20), 87 (100), 72 (13), 70 (13), 56 (29), 55 (29), 41 (33). - 21. - 158 (M^+ + H, 1), 140 (1), 125 (1), 100 (4), 86 (17), 83 (3), 73 (100), 69 (4), 55 (8), 41 (14). - 22. - 141 (M^+ , 21), 126 (6), 124 (9), 109 (16), 98 (25), 83 (21), 82 (33), 73 (72), 69 (78), 67 (30), 55 (43), 42 (61), 41 (100), 39 (41). - 23. - 283 (M^+ , <1), 266 (8), 170 (0.2), 142 (0.4), 128 (4), 111 (2), 100 (5) 97 (2), 86 (8), 83 (4), 73 (100), 70 (6), 57 (17), 43 (13), 41 (8). - 24. - 121 (M^+ , 83), 120 (16), 104 (19), 103 (51), 94 (40), 89 (12), 78 (100), 77 (96), 76 (53), 66 (47), 65 (27), 51 (74), 50 (43), 39 (18). - 25. - 147 (M^+ , 43), 146 (100), 130 (91), 129 (27), 115 (18), 103 (28), 102 (16), 91 (9), 77 (36), 65 (8), 63 (8), 51 (24), 39 (9). - 26. - 179 (M^+ , 40), 164 (13), 162 (75), 150 (100), 147 (15), 146 (16), 134 (36), 133 (52), 132 (79), 120 (22), 118 (19), 105 (18), 91 (31), 79 (30), 77 (28), 67 (15), 65 (19), 55 (25), 53 (27), 41 (48), 39 (32). - 27a. - 239 (M^+ , 1), 222 (16), 210 (15), 208 (10), 192 (32), 171 (9), 166 (90), 154 (8), 150 (14), 148 (36), 136 (9), 132 (20), 120 (28), 118 (23), 110 (35), 98 (99), 93 (27), 91 (29), 79 (34), 69 (27), 67 (39), 59 (20), 55 (25), 53 (29), 41 (100).

HYDROQUINOLINES

The separation of the first distillation range by column chromatography (hexane/ether 2:1) allowed to enrich two further nitrogen-containing constituents of molecular weights 193 and 175, respectively. the compound with shorter retention time showing an elementary composition of $C_{13}H_{23}N$ could be isolated by preparative GC in an amount of 2 mg and based on its spectral data, the structure of the 1, 2, 5, 5-tetramethyl-octahydroquinoline 32 could be proposed (figure 7).

Trying to verify this structure by synthesis, the diketone 28 was converted to its dioxime 29 which cyclized spontaneously to the 2, 5, 5-trimethyl-5, 6, 7, 8-tetrahydroquinoline (31) on treatment with diluted hydrochloric acid. The diketone 28 was obtained as described in literature [12] by titanium (IV)-promoted reaction of 3, 3-dimethyl-1-trimethylsiloxy-cyclohexene with methyl vinyl ketone ethylene acetal and subsequent acid treatment. The final transformation of 31 to 32 by N-methylation and selective hydrogenation could not be realized yet. The tetrahydroquinoline 31,

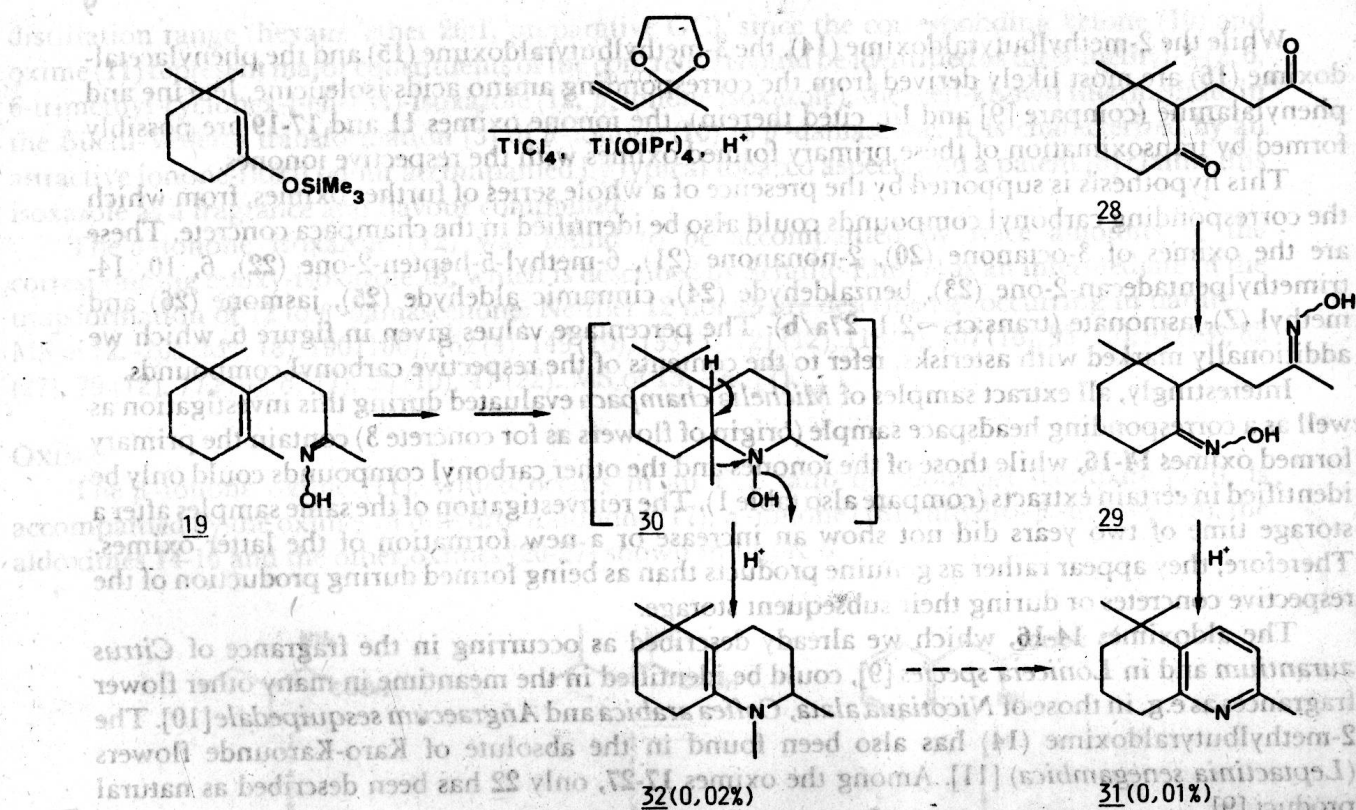


Figure 7. Hydroquinolines 31 and 32.

however, proved to be identical with the second compound of molecular weight 175 present in the same fraction.

This new compound (31) is characterized by an interesting quinoline-like, leathery odour accompanied by ionone aspects. It represents most likely a metabolite of the proposed N-methylated octahydroquinoline 32. The latter might be biologically formed from dihydro- β -ionone oxime (19) by reduction to the hydroxylamine followed by acid-catalysed ring closure to the N-hydroxy-decahydroquinoline 30 and a concomitant migration of the angular methyl group to nitrogen.

Spectral data of 31 and 32

31. - IR.: 1596, 1570, 1460, 1365, 1320, 1262, 1240, 1205, 1140, 1078, 1055, 970, 825, 750 cm^{-1} .
 - $^1\text{H-NMR}$ (400 MHz): 1.25 (s, 2 \times 3H); 1.66 (m, 2H); 1.89 (m, 2H); 2.48 (s, 3H); 2.88 (t, J ~ 7, 2H); 6.93 (d, J ~ 8, 2H); 7.49 (d, J ~ 8, 2H) δ ppm. - MS.: 175 (M^+ , 15), 160 (100), 142 (12), 141 (19), 132 (6), 131 (9), 117 (5), 103 (2), 91 (5), 77 (5), 65 (3), 51 (2), 39 (4).
32. - IR.: 1655, 1476, 1455, 1372, 1313, 1275, 1220, 1200, 1135, 1080, 1065, 978, 950, 922, 857 cm^{-1} .
 - $^1\text{H-NMR}$ (400 MHz): 0.61 (d, J ~ 7, 3H); 0.64 (s, 3H); 0.95 (s, 3H); 1.23 (m, 1H); 1.38 (m, 1H); 1.45-1.65 (m, 4H); 1.76-1.96 (m, 3H); 2.05 (s, 3H); 2.40 (t, J ~ 8, 2H) δ ppm. - MS.: 193 (M^+ , 22), 178 (19), 164 (22), 150 (81), 136 (18), 123 (31), 122 (66), 110 (91), 109 (62), 108 (87), 96 (28), 94 (26), 82 (51), 81 (28), 79 (20), 67 (43), 55 (57), 42 (48), 41 (100), 39 (47).

MONO AND BICYCLIC IONONE DERIVATIVES

Regarding structural variety and richness in carotenoid metabolites, the flower extracts of *Michelia champaca* are comparable with those of tobacco, tea, *Osmanthus fragrans* and *Boronia megastigma*.

Figure 8 summarizes a series of representatives derived from β -ionone.

While the ketones 10 and 35, the alcohols 33 and 36, the epoxy ketone 39, the theaspiranes (43a/b) and the dihydroactinidiolide (44) are well-known natural products, the formates 34 and 37, the β -Ionol 5, 6-epoxide (38), the dihydro- β -ionone 5, 6-epoxide (40) and the epidioxy-alcohol 41 have not been described yet as occurring in nature.

The photocyclization product of β -ionone (42) has also been found in *Osmanthus fragrans* [13].